Electroanalytical Chemistry

by Fred C. Anson

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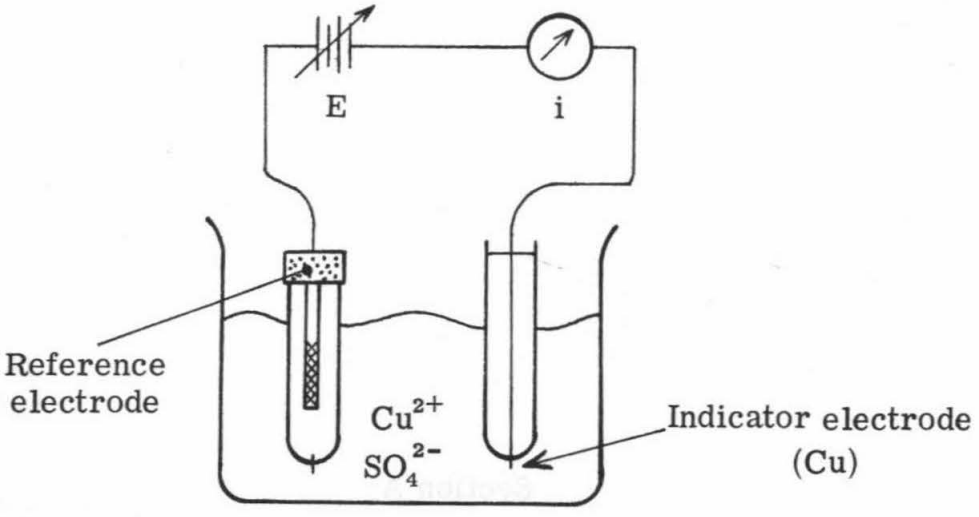
Course Outlin

The final form of this manual and the course content benefitted considerably from extensive criticism by the reviewers of preliminary versions. Although the reviewers' identities were not revealed to me, I had little difficulty in recognizing the style of at least two of them whose comments were particularly helpful. I am extremely grateful to Lou, Don and the other reviewers for their careful, thorough reviews and thoughtful suggestions, most of which were incorporated into the course. I must also record the enormously important contribution of Mrs. Harue Bierce who not only typed countless revisions of the manual but prepared most of the figures and layouts.

Section A

Voltammetry

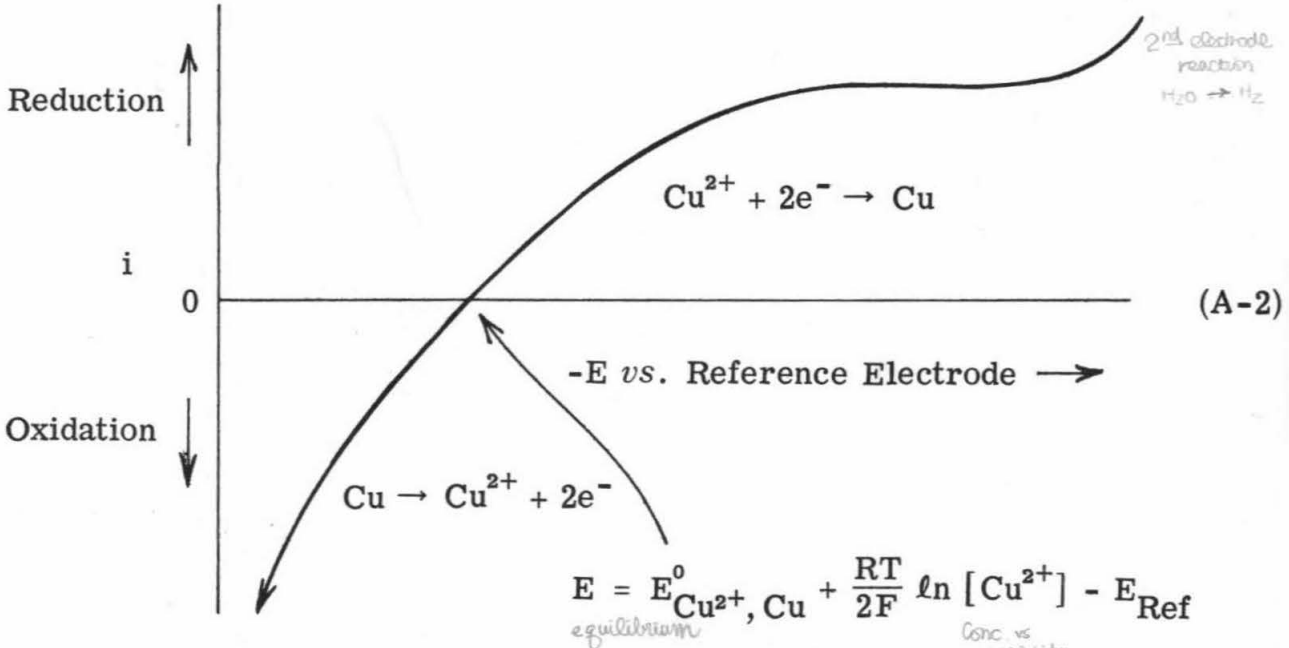
Two-electrode cell



(A-1)

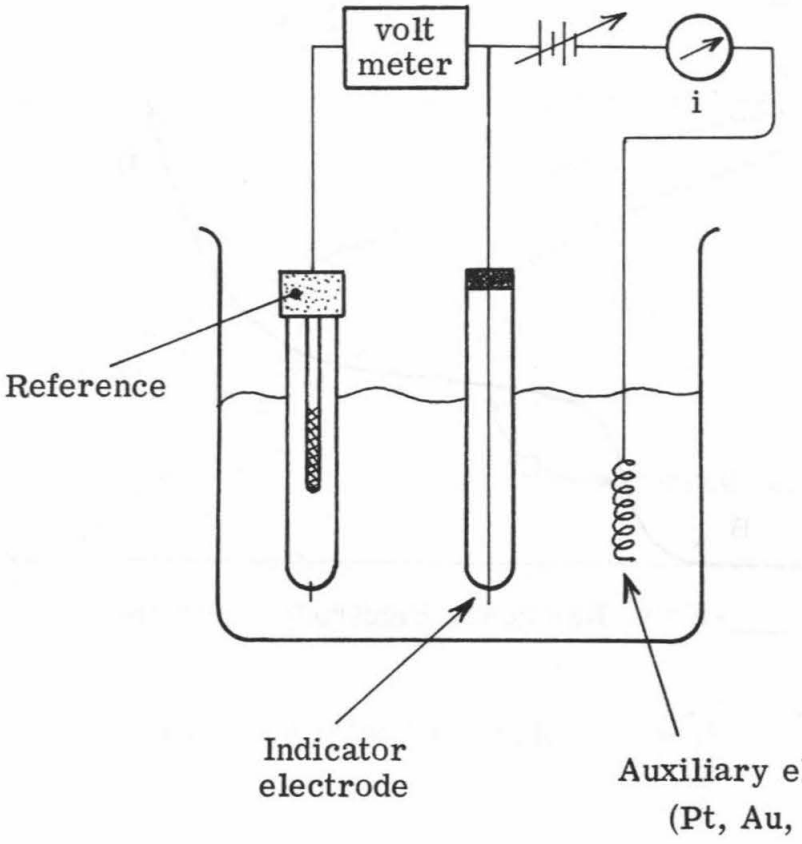
use of Inert electrolyte

A current-potential curve



(A-2)

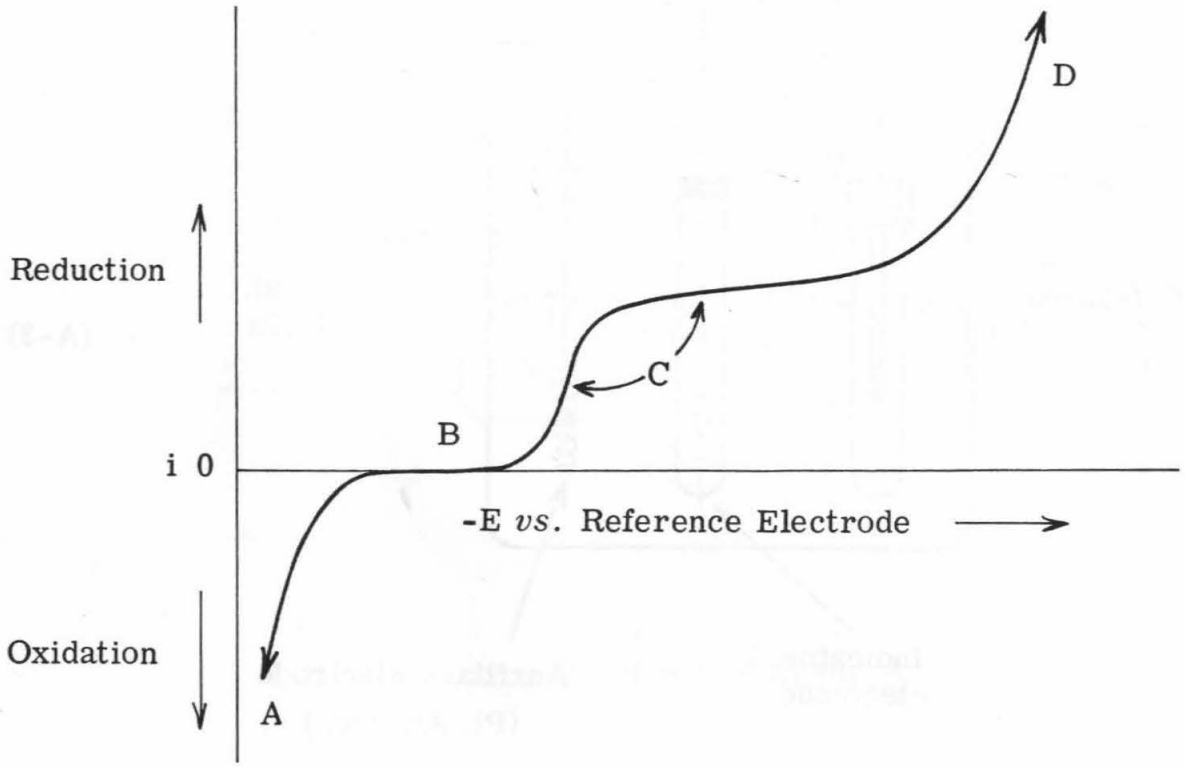
Three-electrode cell



(A-3)

To sort out ohmic-drops

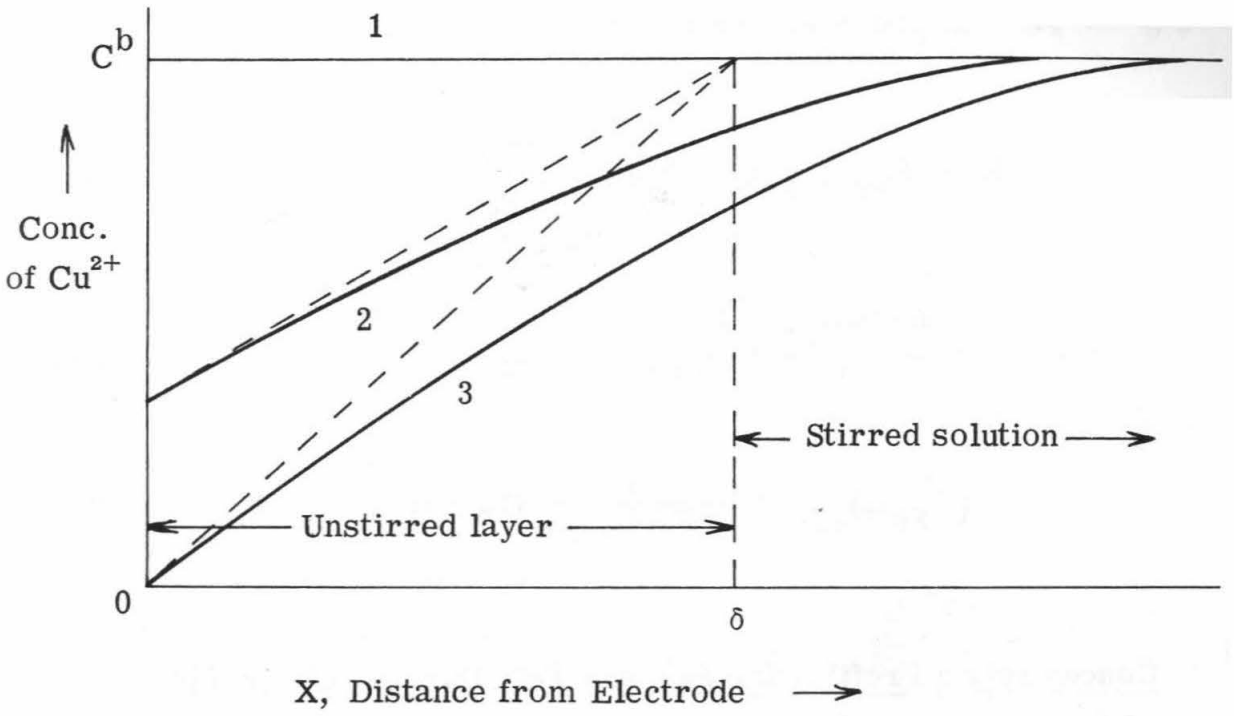
Current-Potential Curve for a Mercury Working Indicator



(A-4)

Region	Electrode Reaction
A	$Hg \rightarrow Hg_2^{2+} + 2e^-$
B	None
C	$Cu^{2+} + 2e^- \xrightarrow{Hg} Cu(Hg)$
D	as in C plus $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Nernst Diffusion Layer



(A-5)

Rate of diffusion: $D\frac{dC}{dX}$ mole cm^{-2} sec^{-1}

$$i = nFAD\left(\frac{dC}{dX}\right)_{X=0} \tag{A-6}$$

If $$\frac{dC}{dX} \sim \frac{C^b - C_{X=0}}{\delta} \tag{A-7}$$

$$i = \frac{nFAD}{\delta}\left(C^b - C_{X=0}\right) \tag{A-8}$$

$$i_\ell = \frac{nFADC^b}{\delta} \tag{A-9}$$

Shapes of current-potential curves:

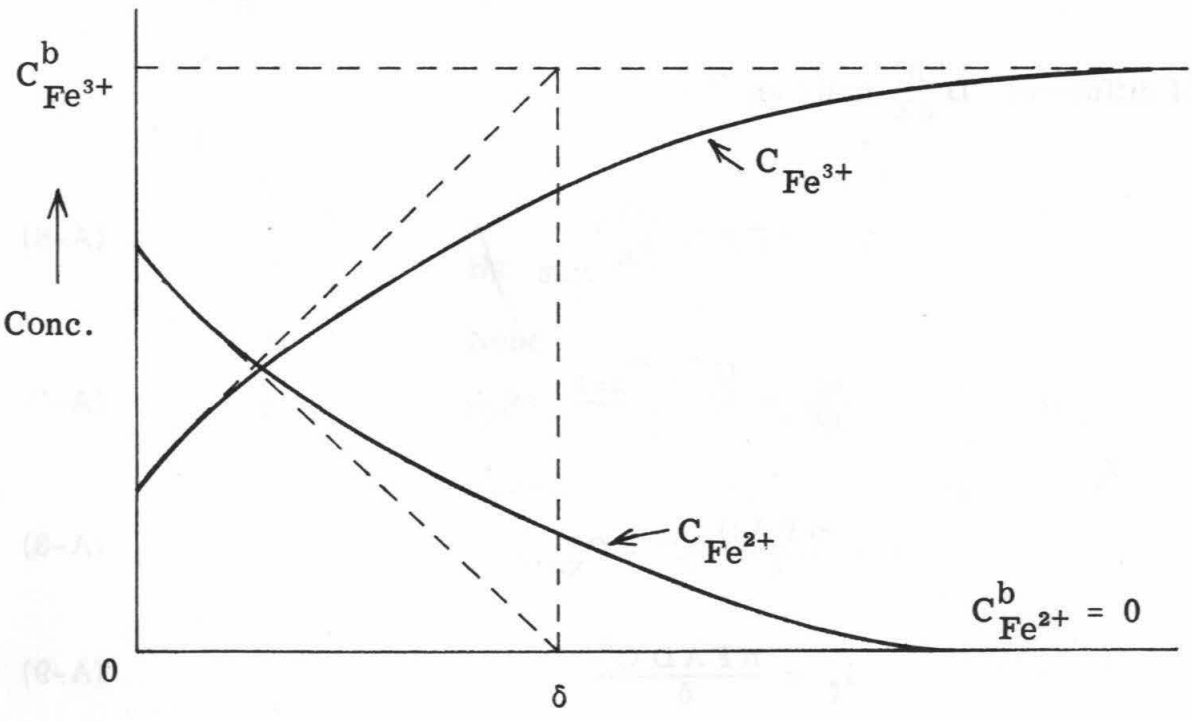
Consider case of Nernstian electrode reaction, e.g., $Fe^{3+} + e^- \rightarrow Fe^{2+}$ at platinum electrodes.

$$E = E^0_{Fe^{3+}, Fe^{2+}} - \frac{RT}{nF} \ell n \frac{(C_{Fe^{2+}})_{X=0}}{(C_{Fe^{3+}})_{X=0}} \qquad \text{(A-10)}$$

$$i = \frac{n F A D_{Fe^{3+}}}{\delta} \left[C^b_{Fe^{3+}} - (C_{Fe^{3+}})_{X=0} \right] \qquad \text{(A-11)}$$

$$(C_{Fe^{3+}})_{X=0} = \frac{\delta}{n F A D_{Fe^{3+}}} (i_\ell - i) \qquad \text{(A-12)}$$

Concentration Profiles for Fe^{3+} and Fe^{2+} During Current Flow



(A-13)

Concentration gradient of Fe^{2+} at surface $= \dfrac{(C_{Fe^{2+}})_{x=0}}{\delta}$ (A-14)

$$i = \frac{n F A D_{Fe^{2+}}}{\delta} (C_{Fe^{2+}})_{x=0} \quad \text{(A-15)}$$

So $$(C_{Fe^{2+}})_{x=0} = \frac{\delta}{n F A D_{Fe^{2+}}} i \quad \text{(A-16)}$$

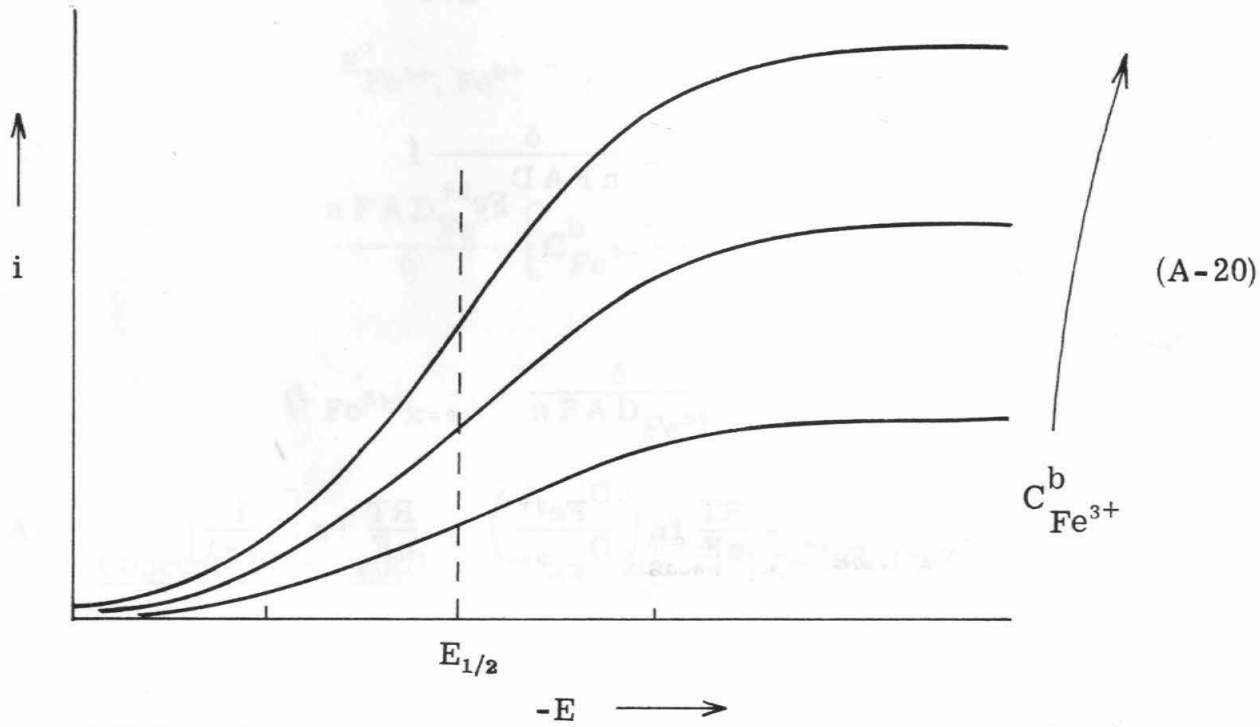
Hence

$$E = E^0_{Fe^{3+}, Fe^{2+}} - \frac{RT}{nF} \ell n \left(\frac{D_{Fe^{3+}}}{D_{Fe^{2+}}} \right) - \frac{RT}{nF} \ell n \left[\frac{i}{i_\ell - i} \right] \quad \text{(A-17)}$$

$$E = E_{1/2} - \frac{RT}{nF} \ell n \left[\frac{i}{i_\ell - i} \right] \quad \text{(A-18)}$$

with $$E_{1/2} = E^0_{Fe^{3+}, Fe^{2+}} - \frac{RT}{nF} \ell n \left(\frac{D_{Fe^{3+}}}{D_{Fe^{2+}}} \right) \quad \text{(A-19)}$$

Shapes of Current-Potential Curves



Section B

Faraday's Law and Controlled Potential Electrolysis

Faraday's Law:

$$\text{Electrical Charge} = nF \times \text{Chemical Change} \qquad \text{(B-1)}$$

Faraday's constant, "the faraday"

F = 96,484 coulombs/mole of electron

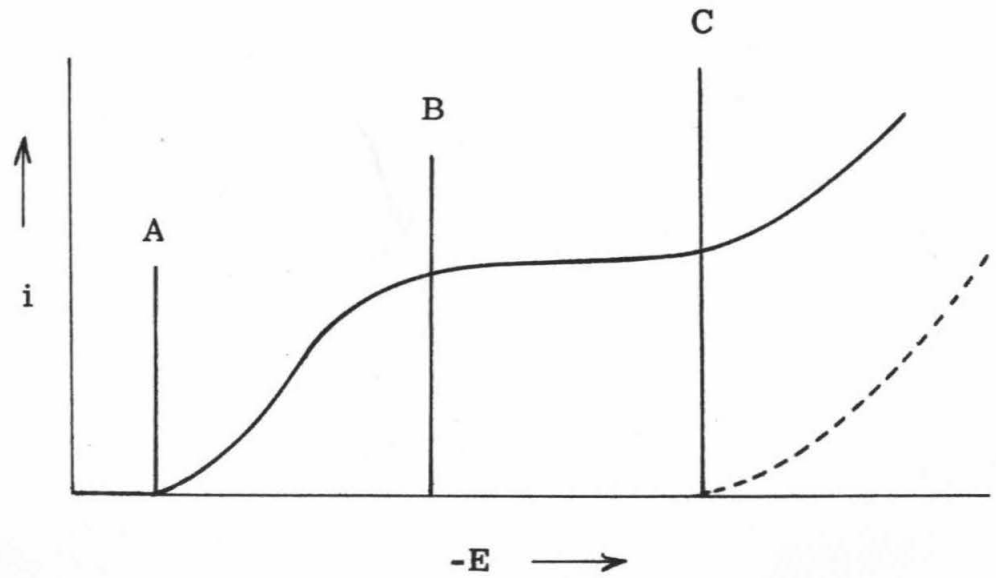
= 96,484 ampere-seconds/mole of electrons

n = moles of electrons per mole of chemical change

Faradaic Efficiency:

$$\text{Faradaic Efficiency} = \frac{\text{Moles of Chemical Change} \times n \times F}{\text{Total Electrical Charge Passed}} \qquad \text{(B-2)}$$

Estimation of Faradaic Efficiency from Current-Potential Curves



(B-3)

Coulometry:

$$Q = \int i\,dt = NnF \qquad \text{(B-4)}$$

Total electrical charge; moles of reactant; Faradays per mole

Current-Time Behavior During Controlled Potential Electrolysis in Stirred Solutions:

$$\text{Rate of supply of electrical charge} = i = \frac{nFADC^b}{\delta} \text{ coul sec}^{-1} \qquad \text{(B-5)}$$

$$\text{Rate of chemical change} = nV\left(\frac{dC^b}{dt}\right) \text{ faradays sec}^{-1} = FnV\left(\frac{dC^b}{dt}\right) \text{ coul sec}^{-1} \qquad \text{(B-6)}$$

(V: volume of solution)

$$-FnV\left(\frac{dC^b}{dt}\right) = \frac{nFADC^b}{\delta} = i \qquad \text{(B-7)}$$

Integrating:

$$C^b = C_o^b \exp(-kt) \qquad \text{(B-8)}$$

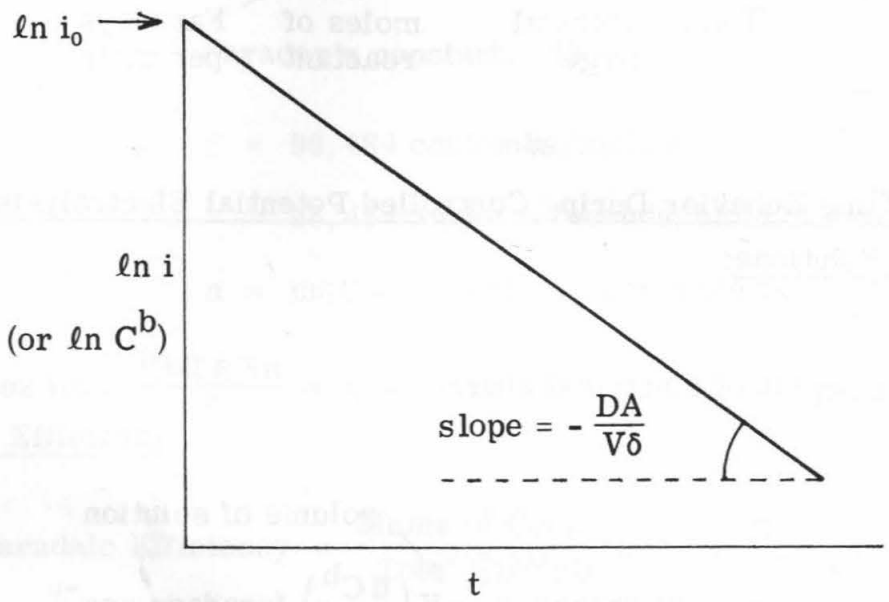
(C_o^b: initial conc.)

$$i = i_o \exp(-kt) \qquad \text{(B-9)}$$

(i_o: initial current)

$$k = \frac{AD}{V\delta} \qquad \text{(B-10)}$$

Logarithmic Decay of Current During Controlled Potential Electrolysis



(B-11)

Typical values of parameters determining slope:

$D = 10^{-5}$ cm^2 sec^{-1} $\quad A = 50$ cm^2

$V = 50$-100 ml $\quad \delta = 2\text{-}4 \times 10^{-3}$ cm

$\frac{DA}{V\delta}$ { 0.0025 to 0.005 sec^{-1} ; 0.15 to 0.30 min^{-1}

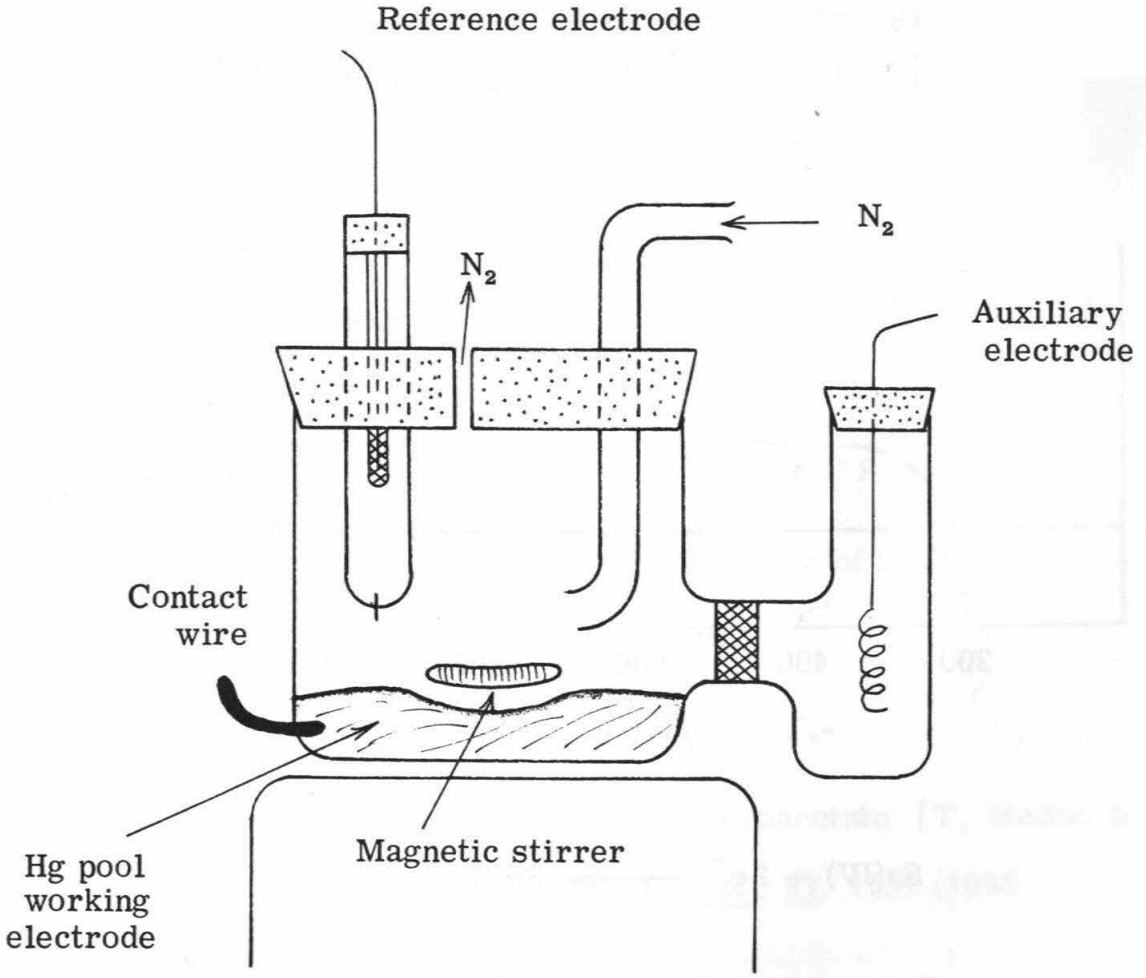
Current *vs.* Time During a Controlled Potential Electrolysis

$k = 0.225$ min^{-1}; $C_0^b = 10^{-2}$ M; $n = 2$

Time, min	Current, milliamp	Per cent of Reactant consumed
0	322	0
1	257	20
2	205	36
5	104	68
10	34	89
20	3.6	99
30	0.38	99.9+

(B-12)

Two-Compartment Cell for
Controlled Potential Electrolysis

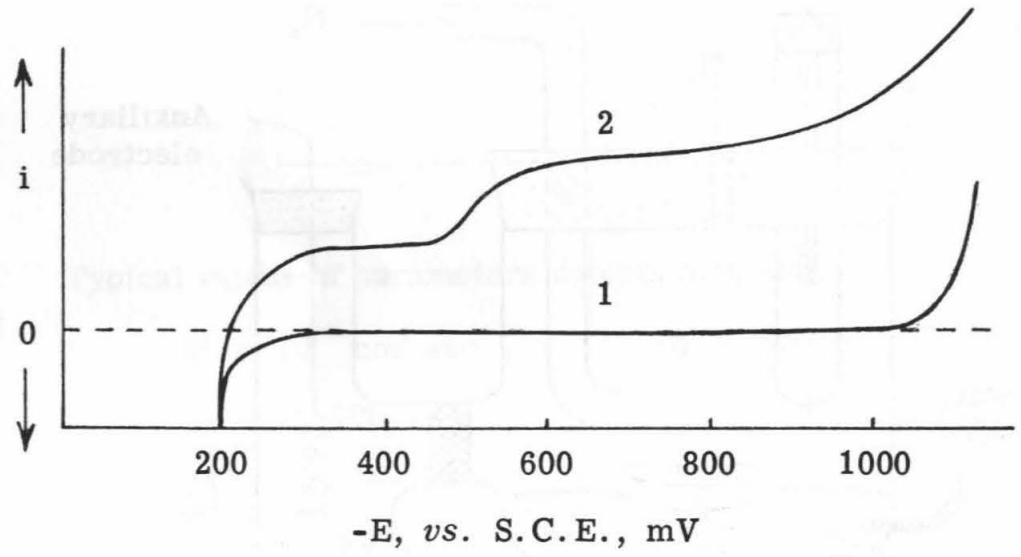


(B-13)

Analytical Coulometry:

$$N = \frac{Q}{nF} \tag{B-14}$$

Example: Determination of Sn(IV)
[A. J. Bard, Anal. Chim. Acta, 22, 577 (1960)]



(B-15)

$$Sn(IV) + 2e^- \longrightarrow Sn(II) \tag{B-16}$$

$$Sn(IV) + 4e^- \xrightarrow{Hg} Sn(Hg) \tag{B-17}$$

Coulometric Data for Sn Determination

Sn taken, mg	Coulombs consumed at -700 mV	Sn found, mg
46.02	149.87	46.09
46.02	150.65	46.33
46.02	149.06	45.85

(B-18)

Sample calculation using Equation (B-14)

Q = coulombs consumed = 149.87 coul.

n = coulombs per mole of Sn(IV) reduced at -700 mV = 4

F = 96,484 coulombs per equivalent

$$\frac{Q}{nF} = \frac{149.87}{4 \times 96,484} = 3.883 \times 10^{-4} \text{ moles of Sn(IV)}$$

$$3.883 \times 10^{-4} \times 118.7 = 46.09 \text{ mg of Sn}$$

(118.7: atomic weight of Sn)

Example: Determination of trichloroacetate [T. Meites & L. Meites, Anal. Chem., 27, 1531 (1955)]

$$CCl_3COO^- + H_2O + 2e^- \longrightarrow CHCl_2COO^- + Cl^- + OH^- \qquad \text{(B-19)}$$

(-900 mV *vs.* S.C.E. at Hg pool)

No interference from $CHCl_2COO^-$, CH_2ClCOO^-, CH_3COO^-

Example: Determination of chromium

[L. Meites, Anal. Chim. Acta, 18, 364 (1958)]

Step I

$$\left.\begin{array}{l} Cr(VI) + 4e^- \\ Cr(III) + e^- \end{array}\right\} \quad \begin{array}{l} -1100 \text{ mV } vs. \text{ SCE} \\ 6 \text{ F HCl} \longrightarrow Cr^{2+} \\ \text{Hg pool} \end{array} \qquad \text{(B-20)}$$

Faradaic efficiency $< 100\%$

Step II

$$Cr^{2+} - e^- \xrightarrow[-400 \text{ mV } vs. \text{ S.C.E.}]{} Cr^{3+} \qquad \text{(B-21)}$$

Faradaic efficiency = 100%

Accuracy $\sim \pm 0.1\%$ for > 0.1 mg of Cr

$\sim \pm 1\%$ for ~ 5 μg of Cr

Some Analytical Advantages of Controlled Potential Coulometry:

- High selectivity via control of electrode potential.
- An "absolute" method--no calibration or standard solutions required.
- High inherent precision and accuracy. Usually superior to methods based on diffusion limited currents, e.g., polarography.

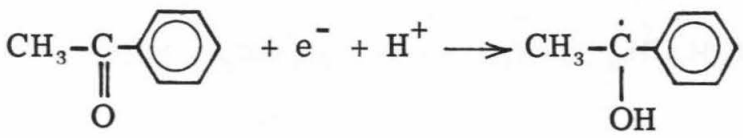
Disadvantages:

- Electrical efficiencies below 100% cause errors.
- Lengthy electrolysis times are sometimes required.

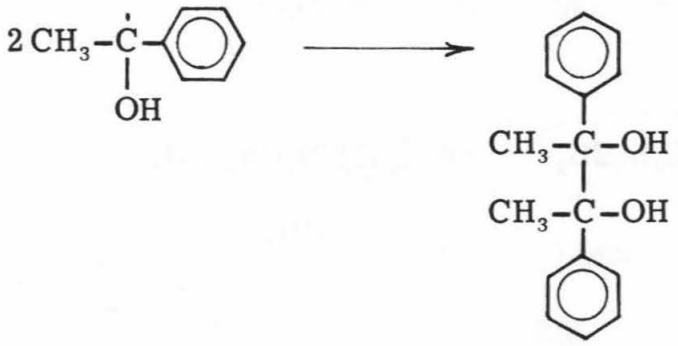
Diagnostic Coulometry:

$$n = \frac{Q}{NF} \qquad \text{(B-22)}$$

Example: Reduction of acetophenone

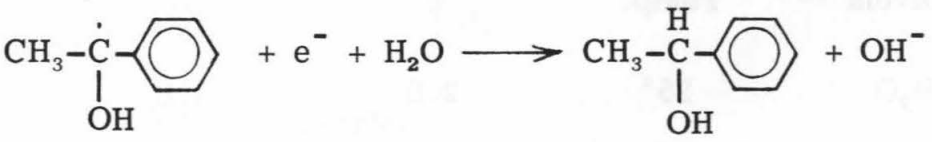


(B-23)



(B-24)

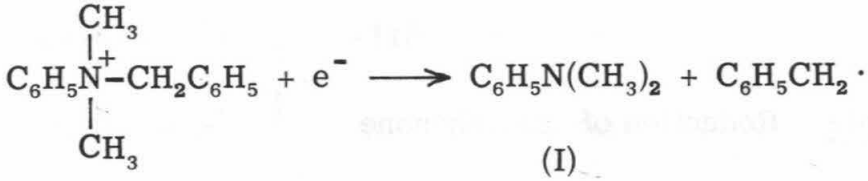
or



(B-25)

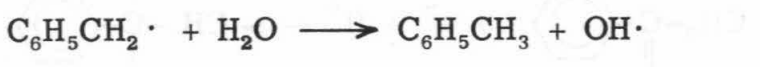
Example: Reduction of benzyldimethylanilinium cation

[J. S. Mayell and A. J. Bard, J. Amer. Chem. Soc., 85, 421 (1963)]



(B-26)

(I)

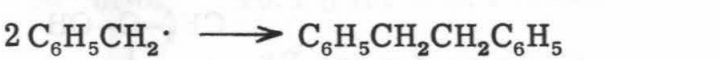


(B-27)

(II)

(B-28)

or



(B-29)

(III)

Coulometric Results

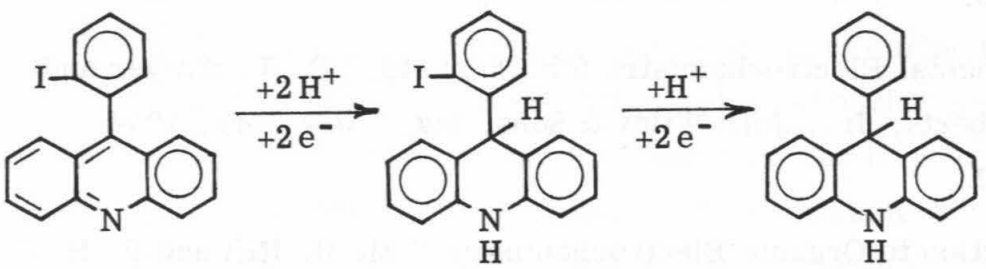
Solvent	Temp.	*n*	Products
H_2O	25°	2.0	I, II
CH_3CN	-35°	1.4-1.9	I, II, III

(B-30)

Synthetic Exploitation of Controlled Potential Electrolysis:

Example: Selective reduction of iodophenyl acridine

[J. J. Lingane *et al.*, J. Amer. Chem. Soc., 65, 1348 (1943)]



(B-31)

I II III

Example: Electrosynthesis of tetraethyl lead

[H. E. Ulery, J. Electrochem. Soc., 116, 1201 (1969)]

$$4\,CH_3CH_2Br + 4\,e^- \xrightarrow[CH_3CN]{\text{Pb elect}} Pb(C_2H_5)_4 + 4\,Br^- \qquad \text{(B-32)}$$

Very high yields.

General References on Controlled Potential Electrolysis:

1. "Electroanalytical Chemistry," J. J. Lingane, Interscience Publishers, New York, 1958, Chapter XIX.

2. Y. Israel and L. Meites in "Handbook of Analytical Chemistry," L. Meites, Ed., McGraw-Hill Book Co., Inc., New York, 1963, pp. 5-195.

3. "Experimental Electrochemistry for Chemists," D. T. Sawyer and J. L. Roberts, Jr., John Wiley & Sons, Inc., New York, 1974, Chapter 7.

4. "Introduction to Organic Electrochemistry," M. R. Rifi and F. H. Covitz, Marcel Dekker, Inc., New York, 1974.

5. G. A. Rechnitz, "Controlled-Potential Analysis," Macmillan, New York, 1963.

6. P. F. Lott, J. Chem. Educ., 42, A261, A361 (1965).

Study Problems:

1-B. Derive equation B-8 from equation B-7.

2-B. 100 ml of a 0.1 M solution of $CuSO_4$ is electrolyzed at a constant electrode potential where the deposition of copper metal occurs.

a. How many coulombs of electrical charge will be required to deposit all of the copper if the faradaic efficiency is 100%?

b. 2000 coulombs of charge were actually used during the electrolysis. What was the faradaic efficiency achieved during the electrolysis?

c. A constant current of 100 milliamperes was passed through the stirred solution for 50 minutes. If the faradaic efficiency was 98% during this period, what concentration of $CuSO_4$ would be left in the solution?

3-B. Suppose the cell shown in A-3 with a platinum auxiliary electrode is used for the electrolyses in question 2-B. How is the electroneutrality of the solution maintained as the Cu^{2+} ions are removed?

4-B. A chemical coulometer based on the oxidation of hydrazine, N_2H_4, at a platinum anode to produce N_2 and the reduction of water at a platinum cathode to produce H_2, is sometimes used to determine the total charge passed during an electrolysis by measuring the volume of gas evolved.

a. Write the electrode reactions involved in the hydrazine coulometer.

b. What amount of electrical charge would have to be passed through the hydrazine coulometer to produce one liter of gas at standard temperature and pressure?

5-B. When anilinium cations,  , are reduced by controlled-potential electrolysis in water [J. S. Mayell and A. J. Bard, J. Amer. Chem. Soc., 85, 421 (1963)], only one faraday of charge is consumed per mole of anilinium ions. What are the likely products of this electroreduction?

Section C

Coulometric Titrations

Coulometric Titrations

Example: Determination of Fe^{3+} by titration with electrogenerated Ti^{3+}

At electrode: $Ti^{4+} + e^- \longrightarrow Ti^{3+}$ (C-1)

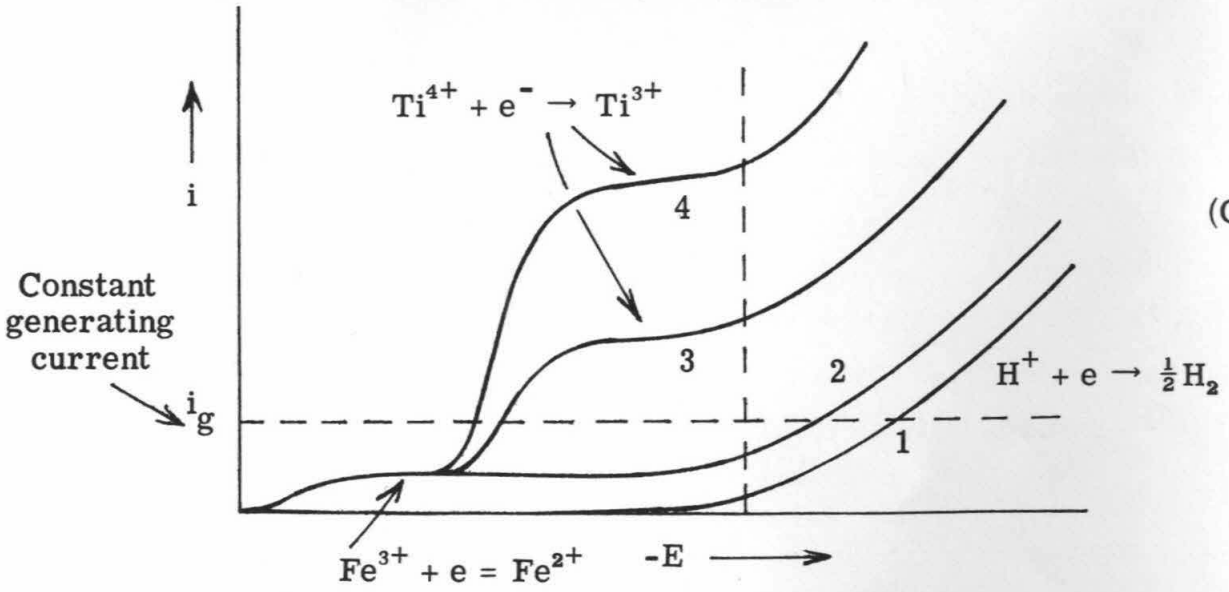
(Ti^{4+}: Titrant precursor)

$(Fe^{3+} + e^- \longrightarrow Fe^{2+})$

In solution: $Ti^{3+} + Fe^{3+} \longrightarrow Ti^{4+} + Fe^{2+}$ (C-2)

(Ti^{3+}: Titrant; Fe^{3+}: Substance to be determined)

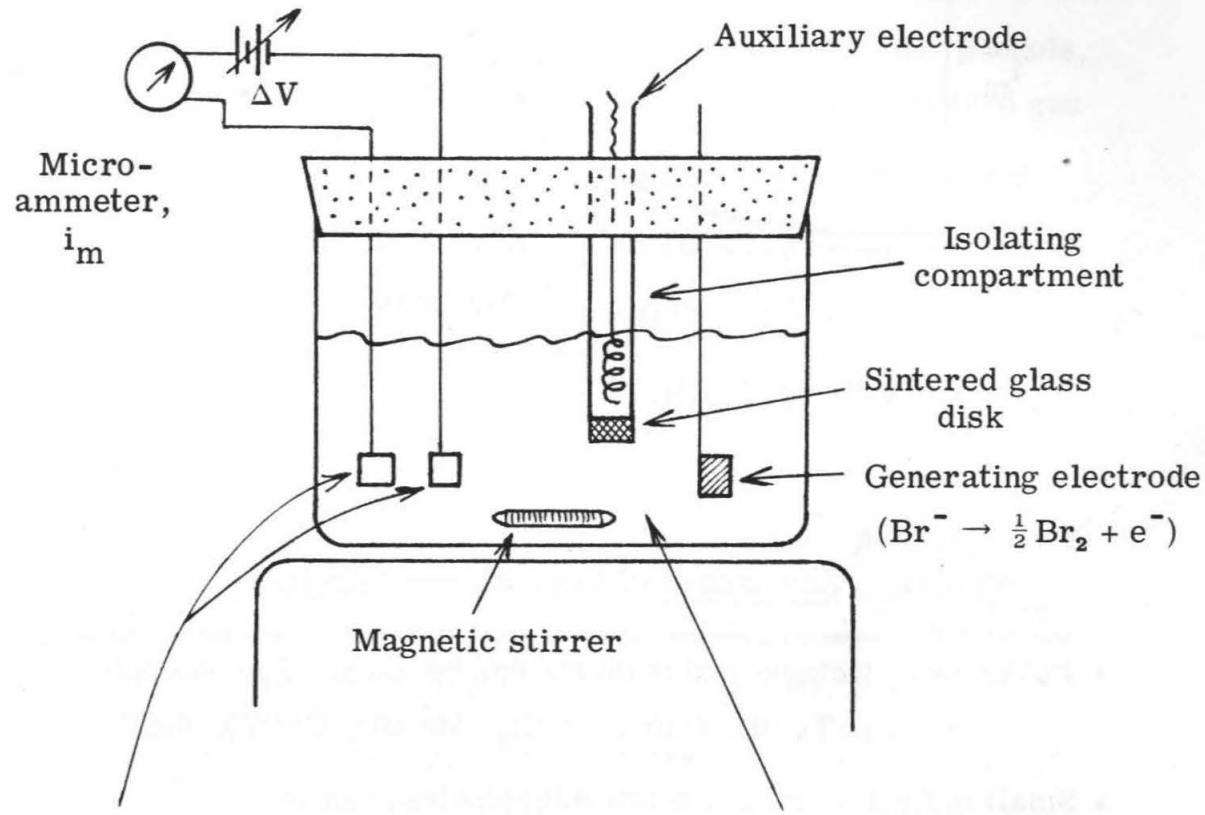
Selecting a Generating Current by Means of Current-Potential Curves



(C-3)

$$N = \frac{i_g t}{nF} = \frac{Q}{nF} \qquad \text{(C-4)}$$

Typical Titration Cell for Coulometric Titrations (C-5)



Amperometric end-point electrodes

(anode: $Br^- \rightarrow \frac{1}{2} Br_2 + e^-$)

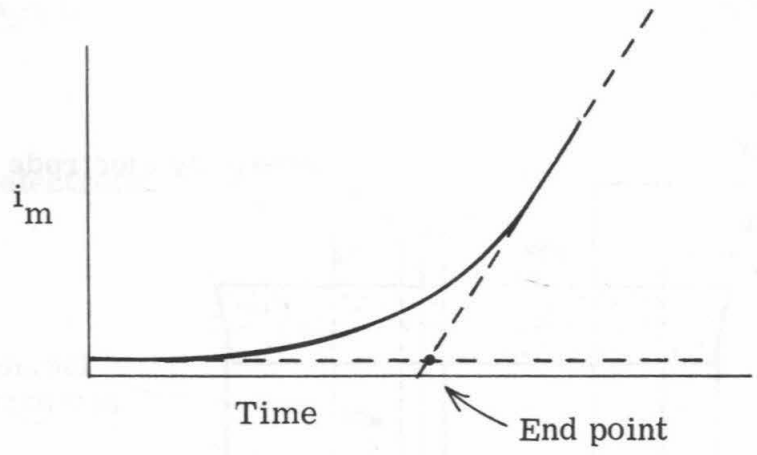
(cathode: $\frac{1}{2} Br_2 + e^- \rightarrow Br^-$)

Solution containing titrant precursor and substance to be determined, e.g., Br^- and As(III), respectively.

Titration Reaction:

$$Br_2 + As(III) \longrightarrow 2\,Br^- + As(V)$$

Amperometric End-Point



(C-6)

Analytical Advantages of Coulometric Titrations (C-7)

- Powerful reductants and oxidants can be used. For example, Cr(II), Ti(III), Cu(I); or Cl_2, Mn(III), Ce(IV), Ag(II).
- Small quantities (e.g., a few micromoles) can be determined accurately and precisely. Quantities as small as a few nanograms have been determined.
- No reagent standardization is needed.
- End point detection is usually simple.
- The method lends itself readily to automation.

Selected Applications of Coulometric Titrations (C-8)

Reagent generated	Substances determined
Br_2	NH_3, As(III), Sb(III), phenols, aniline, olefins, mustard gas
Ag(II)	Ce(III), V(IV), oxalic acid
Ce(IV)	Fe(II), U(IV), hydroquinone
I_3^-	$S_2O_3^{2-}$, S^{2-}, Se(IV)
Ti(III)	Fe(III), V(V), U(VI)
Cu(I)	$Cr_2O_7^{2-}$, IO_3^-
Cr(II)	*p*-nitrophenol, *p*-nitroaniline
Ag(I)	halides, NCS^-, mercaptans
EDTA (from $Hg(EDTA)^{2-}$)	Ca(II), Zn(II), Pb(II), etc.
H^+ (from oxidation of H_2O)	bases
OH^- (from reduction of H_2O)	acids

General References on Coulometric Titrations:

1. "Electroanalytical Chemistry," J. J. Lingane, Interscience Publishers, New York, 1958, Chapters XX and XXI.

2. P. S. Farrington in "Handbook of Analytical Chemistry," L. Meites, Ed., McGraw-Hill Book Co., Inc., New York, 1963, pp. 5-187.

3. "Polarographic Techniques," L. Meites, Interscience Publishers, New York, 1965, p. 546.

4. "Experimental Electrochemistry for Chemists," D. T. Sawyer and J. L. Roberts, Jr., John Wiley & Sons., Inc., New York, 1974, p. 418.

Study Problems:

1-C. Typical values of generating currents and titration times during coulometric titrations are 5 milliamp and 250 seconds, respectively. To what molar quantity of the substance to be determined do these values correspond?

2-C. A typical value of a diffusion limited current density in a stirred solution of a reagent precursor whose electrode reaction involves one Faraday per mole is about 0.5 milliamp cm^{-2} $(millimolar)^{-1}$.
Using this value, try to explain the following observation:
Excellent results were obtained when As(III) was determined in a coulometric titration in which Br_2 was generated from a 0.1 M solution of NaBr at a 0.5 cm^2 platinum anode with a current of 10 milliamperes. However, the results were consistently too high if the current was increased to 30 milliamperes.

3-C. A coulometric titration for NH_3 is based on the reaction:

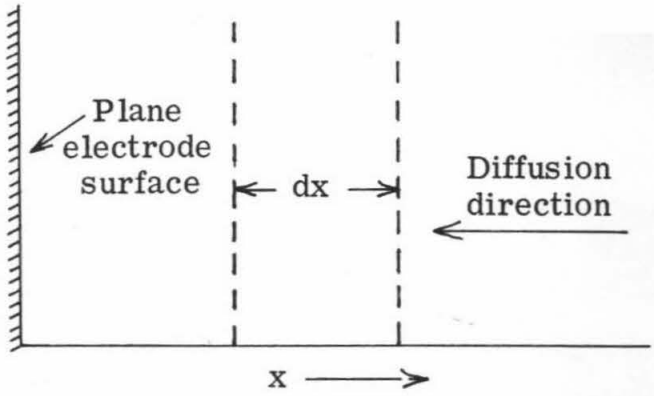
$$2\,NH_3 + 3\,BrO^- \longrightarrow N_2 + 3\,Br^- + 3\,H_2O$$

The BrO^- ion is generated by electro-oxidation of Br^- with a current of 4 milliamperes in a solution buffered near pH 8.5 (cf. C. M. Arcand and E. H. Swift, Anal. Chem., 28, 440 (1963)). Calculate the theoretical titration time for each micromole of NH_3 present.

Section D

Chronoamperometry and Chronocoulometry

Semi-infinite linear diffusion:



(D-1)

Fick's First Law:

Quantity of the diffusing substance which crosses any plane parallel to electrode, that is the flux, (in moles cm^{-2} sec^{-1}) is $D\left(\frac{\partial C}{\partial x}\right)$. D is the diffusion coefficient (cm^2 sec^{-1}) and $\left(\frac{\partial C}{\partial x}\right)$ is the concentration gradient (moles cm^{-4}).

$$\text{flux} = D\left(\frac{\partial C}{\partial x}\right) \tag{D-2}$$

Fick's Second Law:

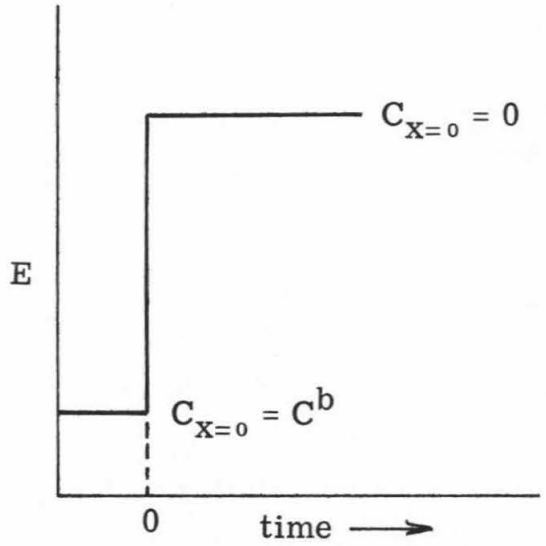
$$\left(\frac{\partial C}{\partial t}\right) = D\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{D-3}$$

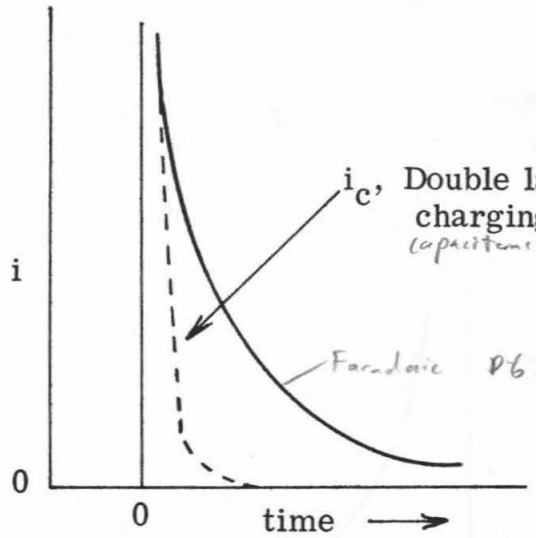
$$\text{Current} = nFA\,(\text{flux})_{X=0} = nFAD\left(\frac{\partial C}{\partial x}\right)_{X=0} \tag{D-4}$$

When $C_{X=0} = 0$; $\left(\frac{\partial C}{\partial x}\right)_{X=0} = \frac{C^b}{(\pi D t)^{1/2}}$ (D-5)

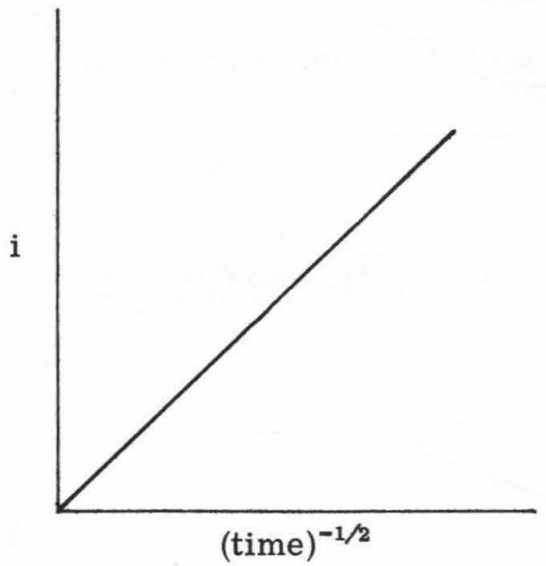
so $i = \frac{nFAD^{1/2}C^b}{(\pi t)^{1/2}}$ Cottrell Equation (D-6)

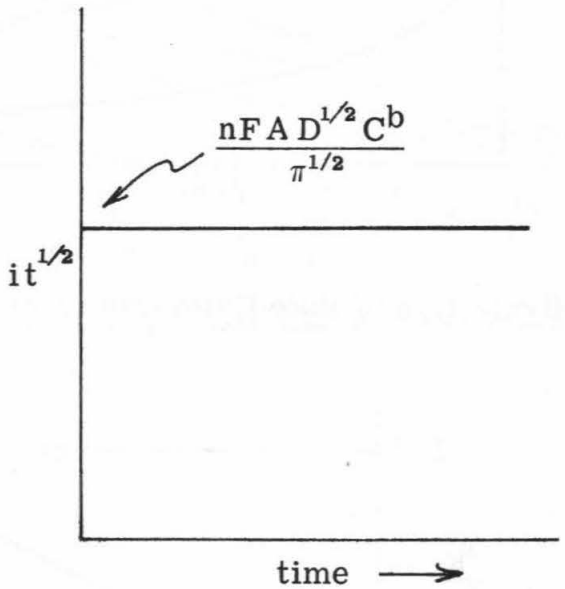
Current-time Responses--Chronoamperometry





(D-7)



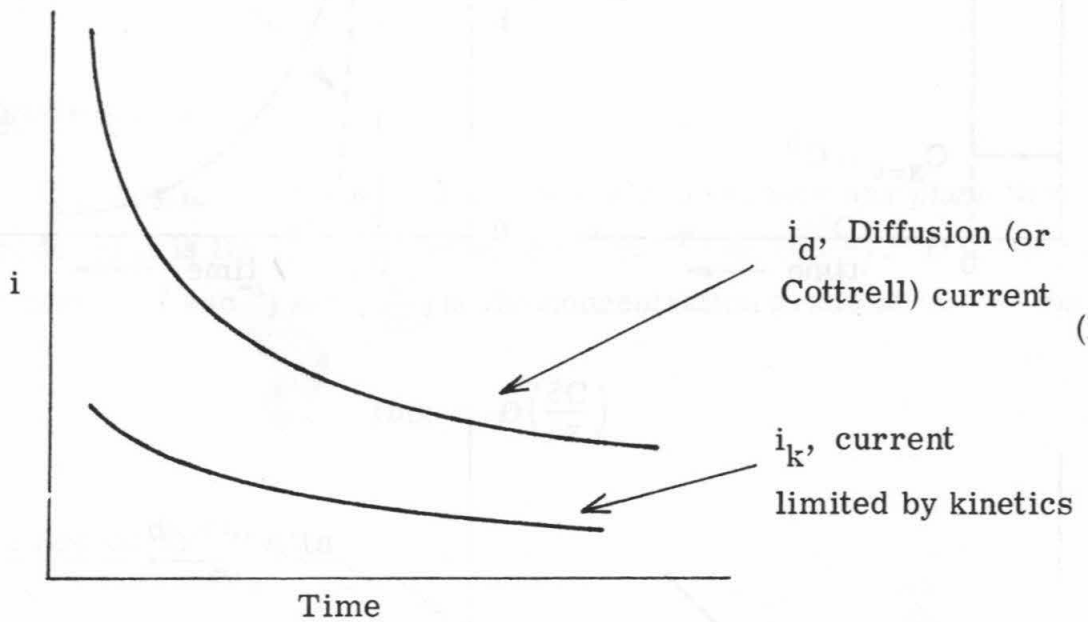


(D-8)

Kinetic Effects in Chronoamperometry

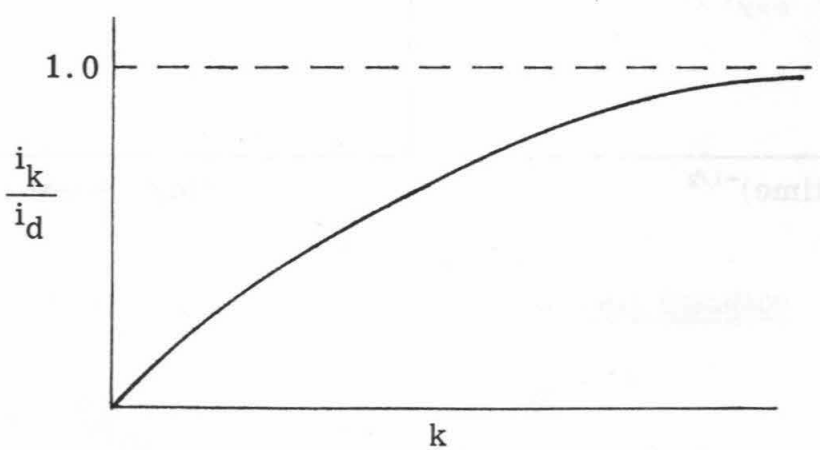
$$Ox + e^- \xrightarrow[\text{slow}]{k} R \qquad \text{(D-9)}$$

$$Z \xrightarrow[\text{slow}]{k} Ox \xrightarrow[\text{fast}]{+e^-} R \qquad \text{(D-10)}$$



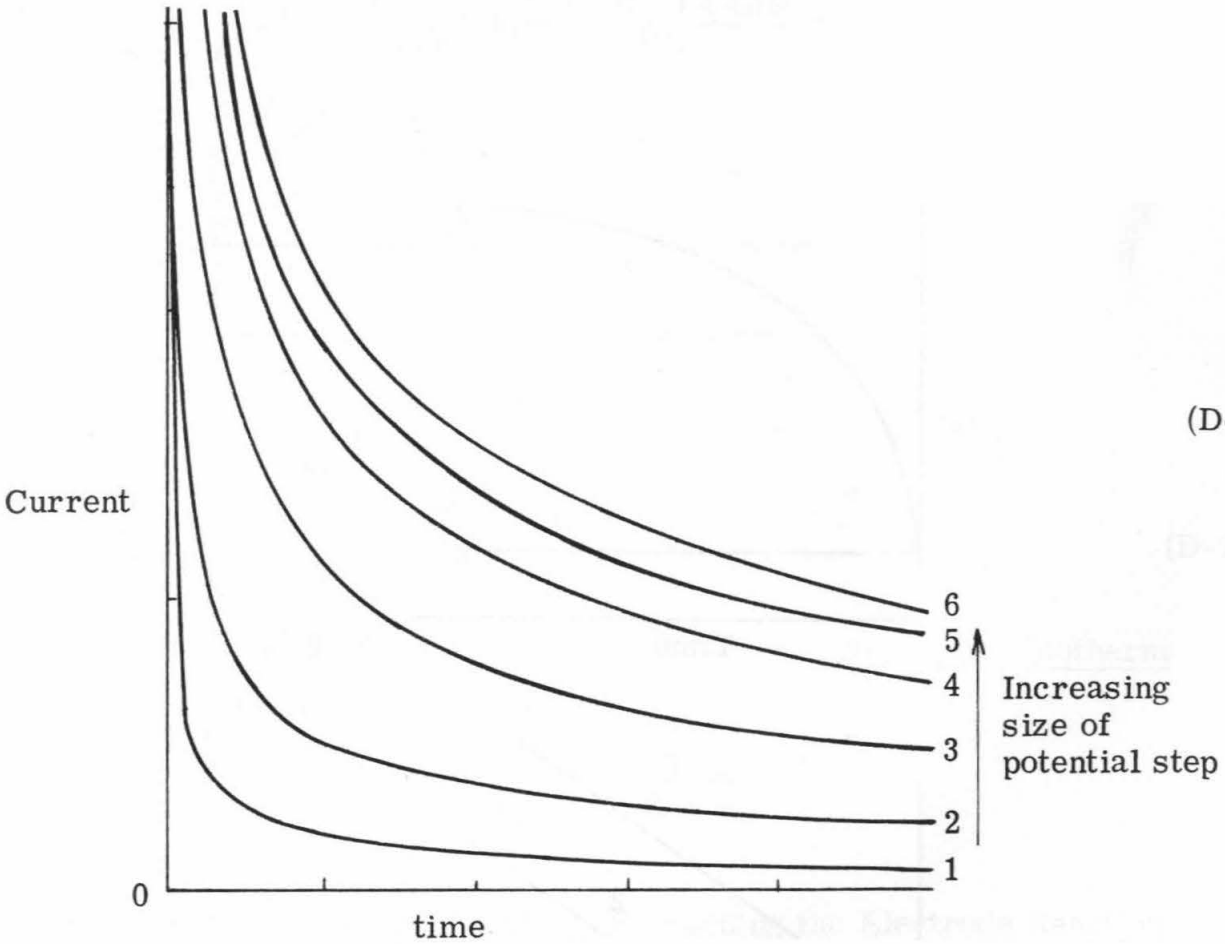
(D-11)

Evaluation of Rate Constants from Kinetically Limited Currents



(D-12)

Potential-dependence of the Chronoamperometric Response



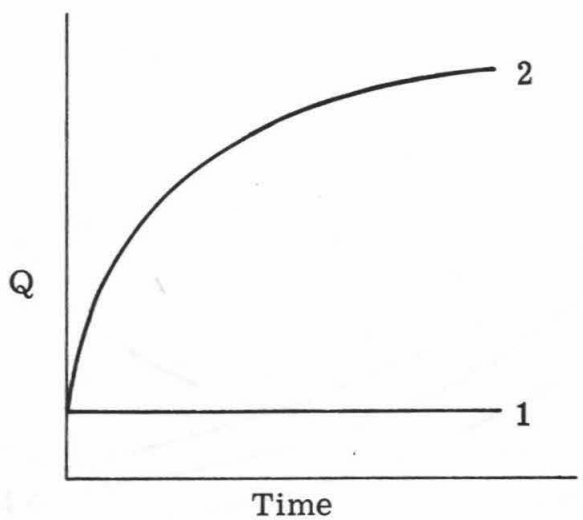
(D-13)

Chronocoulometry:

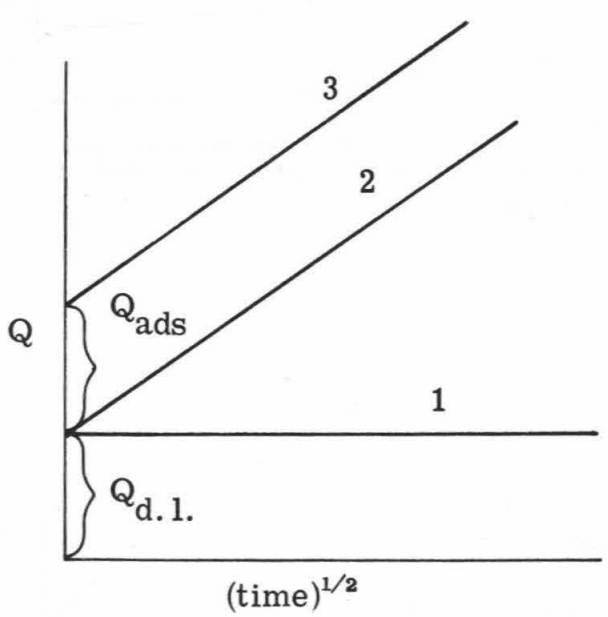
$$Q = \int i\,dt = \frac{nFAC^b D^{1/2}}{\pi^{1/2}} \int t^{-1/2}\,dt + \int i_c\,dt \qquad \text{(D-14)}$$

Double layer charging

$$Q = \frac{2nFAC^b D^{1/2} t^{1/2}}{\pi^{1/2}} + Q_{d.l.} \qquad \text{(D-15)}$$

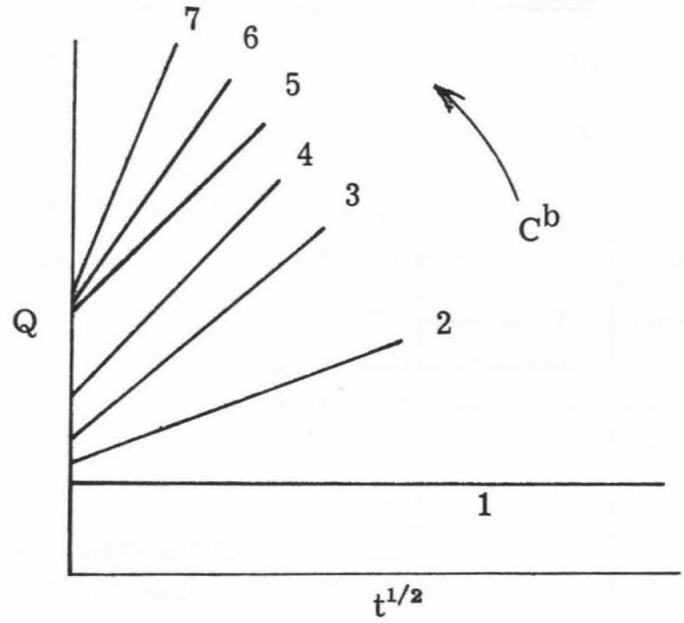


(D-16)

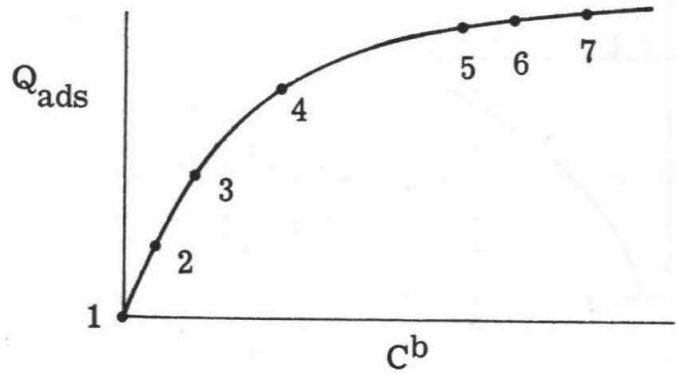


(D-17)

Example: Adsorption of $Cr(OH_2)_3(NCS)_3$ on mercury



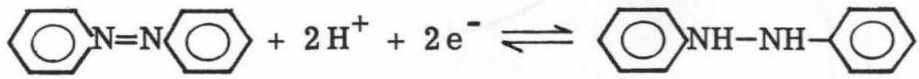
(D-18)



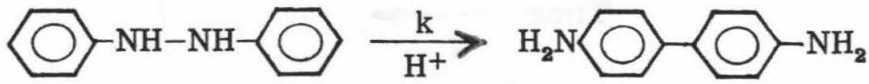
(D-19)

Adsorption Isotherm

Kinetics of a "Follow-up" Reaction Succeeding the Electrode Reaction



(D-20)

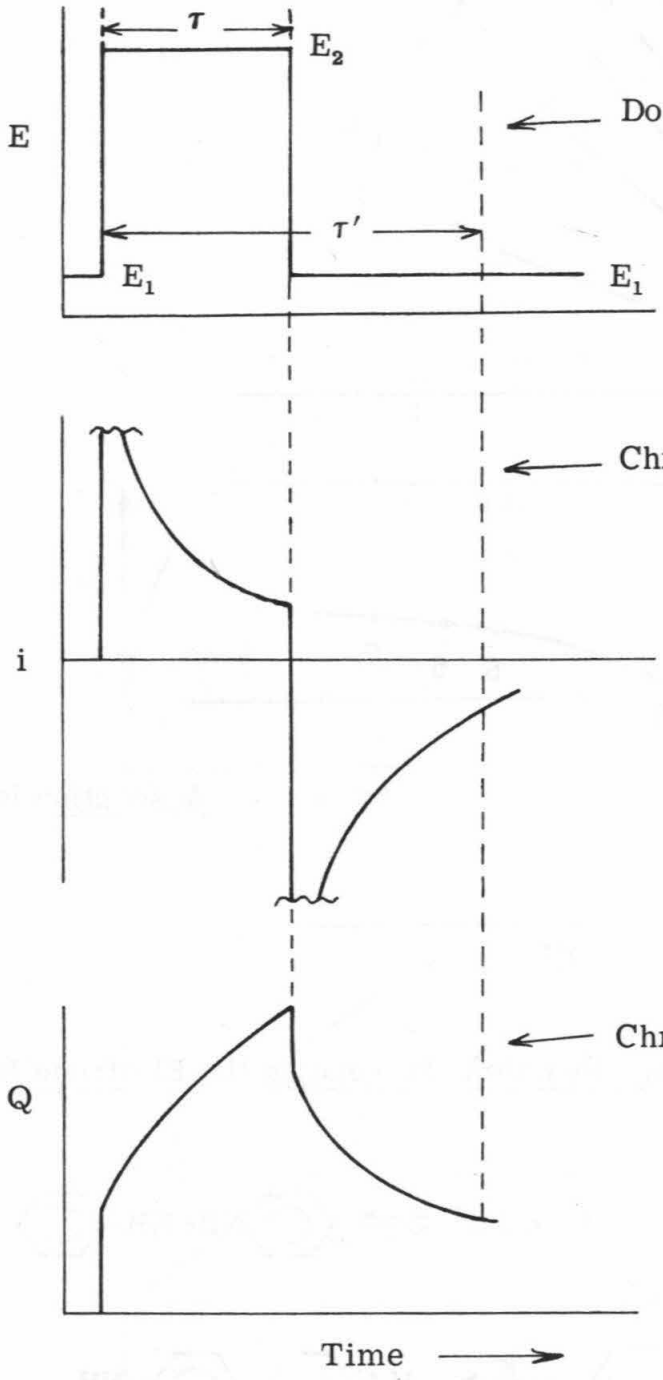


(D-21)

(Benzidine rearrangement)

Double Potential-Step

Chronoamperometry and Chronocoulometry



(D-22)

(D-23)

(D-24)

References on Chronoamperometry and Chronocoulometry:

Chronoamperometry:

1. R. W. Murray, in "Physical Methods of Chemistry, Part IIA: Electrochemical Methods," A. Weissberger and B. W. Rossiter, Eds., Wiley-Interscience, New York, 1971, Ch. VIII.

2. "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Eds., Interscience Publishers, Inc., New York, 1963, Part I, Vol. 4, Chapters 42, 43, 44.

3. "New Instrumental Methods in Electrochemistry," P. Delahay, Interscience Publishers, Inc., New York, 1954.

4. W. M. Schwarz and I. Shain, J. Phys. Chem., 69, 30 (1965).

Chronocoulometry:

5. J. H. Christie, R. A. Osteryoung, and F. C. Anson, J. Electroanal. Chem., 13, 236 (1967).

6. F. C. Anson, J. H. Christie, and R. A. Osteryoung, J. Electroanal. Chem., 13, 343 (1967).

7. R. P. Van Duyne, T. H Ridgeway, and C. N. Reilley, J. Electroanal. Chem., 34, 283 (1972).

8. Also reference 1 above.

Study Problems:

1-D. Fick's Second Law, eqn. (D-2), can easily be derived from Fick's First Law: Consider the volume of solution contained within the layer of thickness dx shown in Fig. (D-1). If its cross sectional area is A,

a. What is the flux, f_x, of material departing from this volume at x?

b. What is the flux, f_{x+dx}, of material entering this volume at x + dx?

c. What is the change in concentration, dC, within this volume in the time interval dt?

d. By noting that $f_{x+dx} = f_x + \left(\frac{\partial f_x}{\partial x}\right)dx$ substitute into the expression obtained in part c to obtain Fick's Second Law.

2-D. During a chronoamperometric experiment with 100 ml of a 0.01 M solution of an oxidant, the measured current was 55 milliamp. 10^{-2} seconds after the experiment commenced.

a. What will be the value of the current after 100 seconds? After 10,000 seconds?

b. What fraction of the original oxidant will be reduced after 100 seconds if a two-electron electrode reaction is involved?

c. Why do the currents become so small even though most of the oxidant has not been reduced?

3-D. Chronoamperometry has frequently been used to measure diffusion coefficients of electroactive species. The following chronoamperometric data were obtained during the reduction of IO_3^- ions to I^- ions at a planar mercury electrode having an area of 0.1 cm^2. The concentration of IO_3^- was 0.1 millimolar.

Time, millisec.	Current, milliamperes
1	340
2	242
5	154
10	107
20	77
50	48
100	34

Estimate the value of the diffusion coefficient of IO_3^- in the solution used for the chronoamperometric experiments.

4-D. A chronocoulometric experiment was conducted with a 1 mM solution of a reactant molecule which adsorbs on the electrode surface to produce a layer in which each adsorbed molecule occupies $100\ \text{Å}^2 = 10^{-14}\ \text{cm}^2$.

a. If the reactant undergoes a two-electron reduction at the electrode, calculate the electrical charge that will be consumed by the reduction of the adsorbed molecules in microcoulombs cm^{-2}.

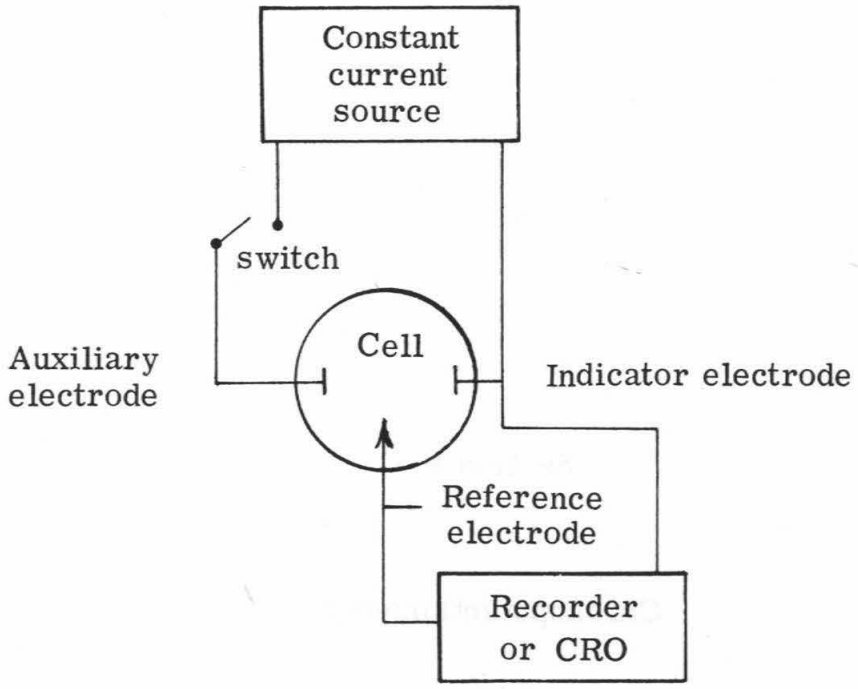
b. If the reactant has a diffusion coefficient of $2 \times 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$ calculate the additional electrical charge that will be consumed by molecules that diffuse to the electrode within 10^{-2}, 10^{-1} and 1 sec.

c. How would the accuracy of measurements of the quantity of adsorbed reactants by chronocoulometry depend on the duration of the chronocoulometric experiment?

Section E

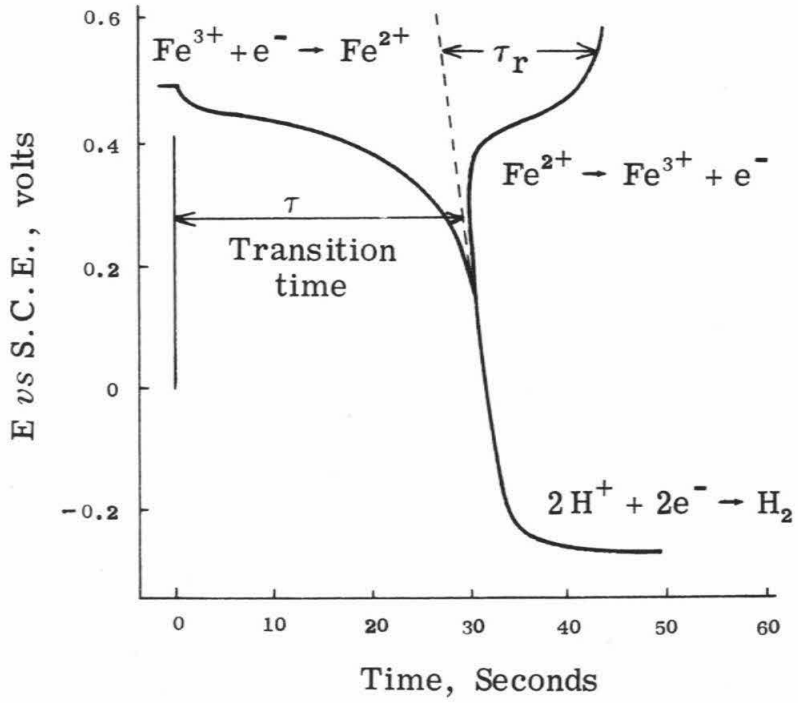
Chronopotentiometry

Experimental Arrangement for Chronopotentiometry



(E-1)

A Chronopotentiogram



(E-2)

$$i = nFAD\left(\frac{\partial C}{\partial x}\right)_{x=0} = \text{constant} \qquad \text{(E-3)}$$

$$C_{x=0} = C^b - \frac{2it^{1/2}}{nFA(\pi D)^{1/2}} \qquad \text{(E-4)}$$

when $C_{x=0} = 0, \quad t \equiv \tau$

$$\tau^{1/2} = \frac{nFA(\pi D)^{1/2} C^b}{2i} \qquad \underline{\text{Sand Equation}} \qquad \text{(E-5)}$$

Analytical Applications of Chronopotentiometry: Determination of Metal Cations by Reduction at Mercury Pool Electrodes: [C. N. Reilley *et al.*, Anal. Chem., 27, 483 (1955)] (E-6)

Metals determined:	Pb^{2+}, Cd^{2+}, Zn^{2+}--singly and in mixtures
Concentration ranges:	0.1 to 10 mM
Transition times:	0.2 to 20 sec
Typical accuracy:	4-5%

Some typical chronopotentiometric analytical results [M. M. Nicholson *et al.*, Anal. Chem., 27, 1095 (1955)]:

Chronopotentiometric Data on Lead Nitrate in 0.2 M Nitric Acid at 25°C (E-7)

C^b, moles per liter	i, ma	τ, seconds	$i\tau^{1/2}/C^b$ amp $sec^{1/2}$ cm^3 $mole^{-1}$ ($\times 10^{+3}$)
1×10^{-4}	0.100	3.1	1.8
2	0.150	4.0	1.51
5	0.250	8.4	1.45
1×10^{-3}	0.450	10.4	1.45
2	1.200	5.48	1.40
5	2.50	8.33	1.44
5	3.00	5.67	1.43
1×10^{-2}	5.00	8.04	1.42
1	5.00	8.26	1.44
2	10.00	8.21	1.43
		Av.	1.44[a]

[a] Omitting the first entry.

Shapes of Chronopotentiograms:

For nernstian systems:

$$E = \underbrace{E^0 - \frac{RT}{nF}\ell n\left(\frac{D_{ox}}{D_{red}}\right)^{1/2}}_{E_{1/4}} - \frac{RT}{nF}\ell n\frac{t^{1/2}}{\tau^{1/2}-t^{1/2}} \qquad \text{(E-8)}$$

1/4 way to transition time

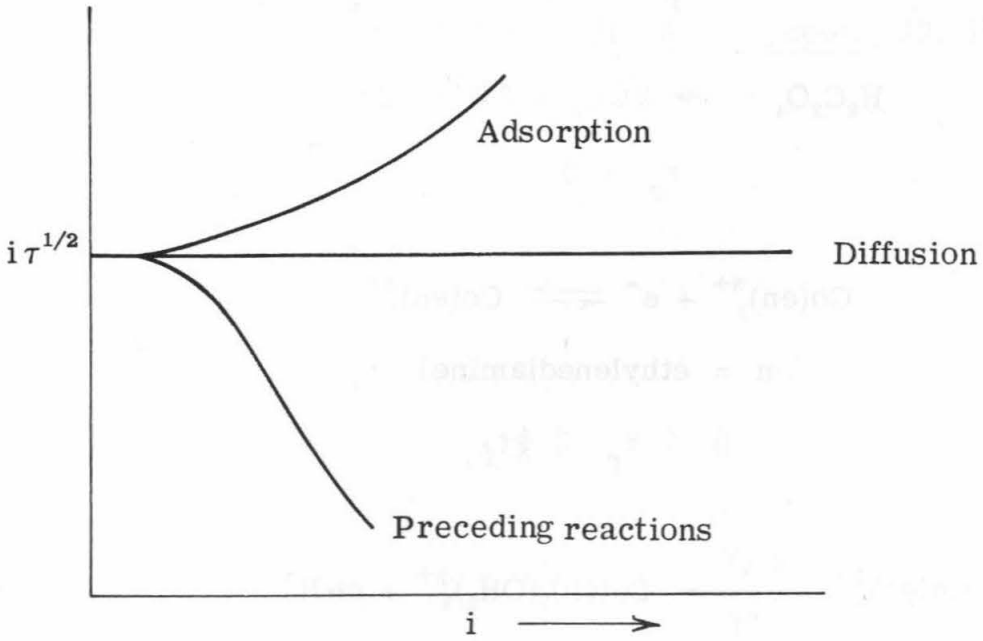
$$E = E_{1/4} - \frac{RT}{nF}\ell n\frac{t^{1/2}}{\tau^{1/2}-t^{1/2}} \qquad \text{(E-9)}$$

Compare $E_{1/4}$ with $E_{1/2}$ for current-potential curves.

Diagnosis of reaction mechanisms by means of chronopotentiometry:

$$i\tau^{1/2} = \frac{nFAC^b}{2}(\pi D)^{1/2} = \text{constant} \qquad \text{(E-10)}$$

A Diagnostic Plot

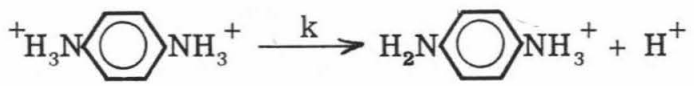


(E-11)

Examples of preceding chemical reactions:

$$Cd(CN)_4^{2-} \xrightarrow{k} Cd(CN)_2 + 2\,CN^- \qquad \text{(E-12)}$$

$$S_2O_4^{2-} \xrightarrow{k} 2\,SO_2^- \cdot \qquad \text{(E-13)}$$



(E-14)

Current reversal chronopotentiometry:

$$\tau_r = \tfrac{1}{3} t_f \qquad (t_f \leq \tau) \qquad \text{(E-15)}$$

Examples:

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$

$$\tau_r = \tfrac{1}{3} t_f \qquad \text{(E-16)}$$

$$H_2C_2O_4 \longrightarrow 2\,CO_2 + 2\,H^+ + 2\,e^-$$

$$\tau_r = 0 \qquad \text{(E-17)}$$

$$Co(en)_3^{3+} + e^- \rightleftharpoons Co(en)_3^{2+} \qquad \text{(E-18)}$$

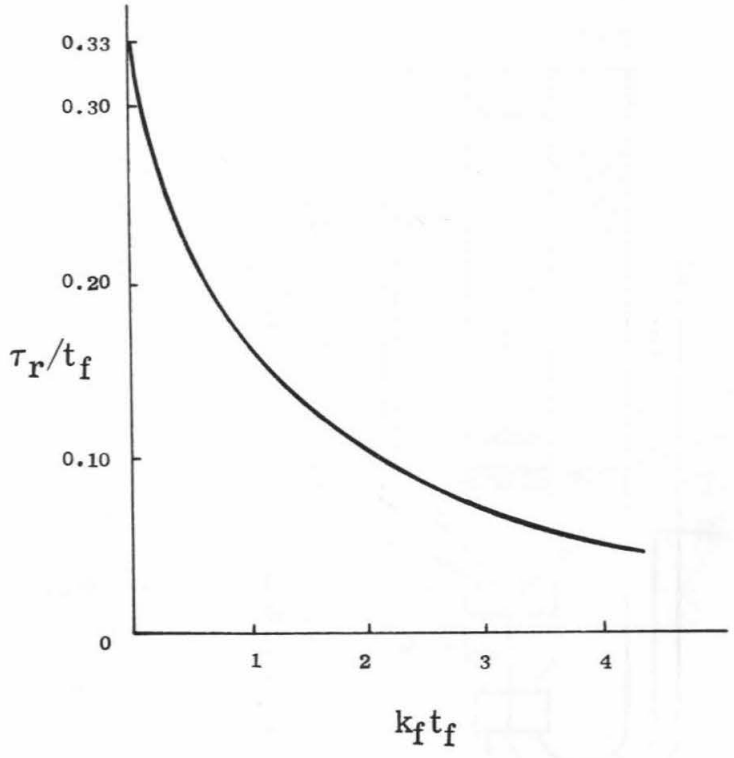
(en = ethylenediamine)

$$0 < \tau_r < \tfrac{1}{3} t_f$$

$$Co(en)_3^{2+} \xrightarrow[k_f]{H_3O^+} Co(en)_2(OH_2)_2^{2+} + en\,H^+ \qquad \text{(E-19)}$$

Evaluation of first-order rate constants from reverse transition times:

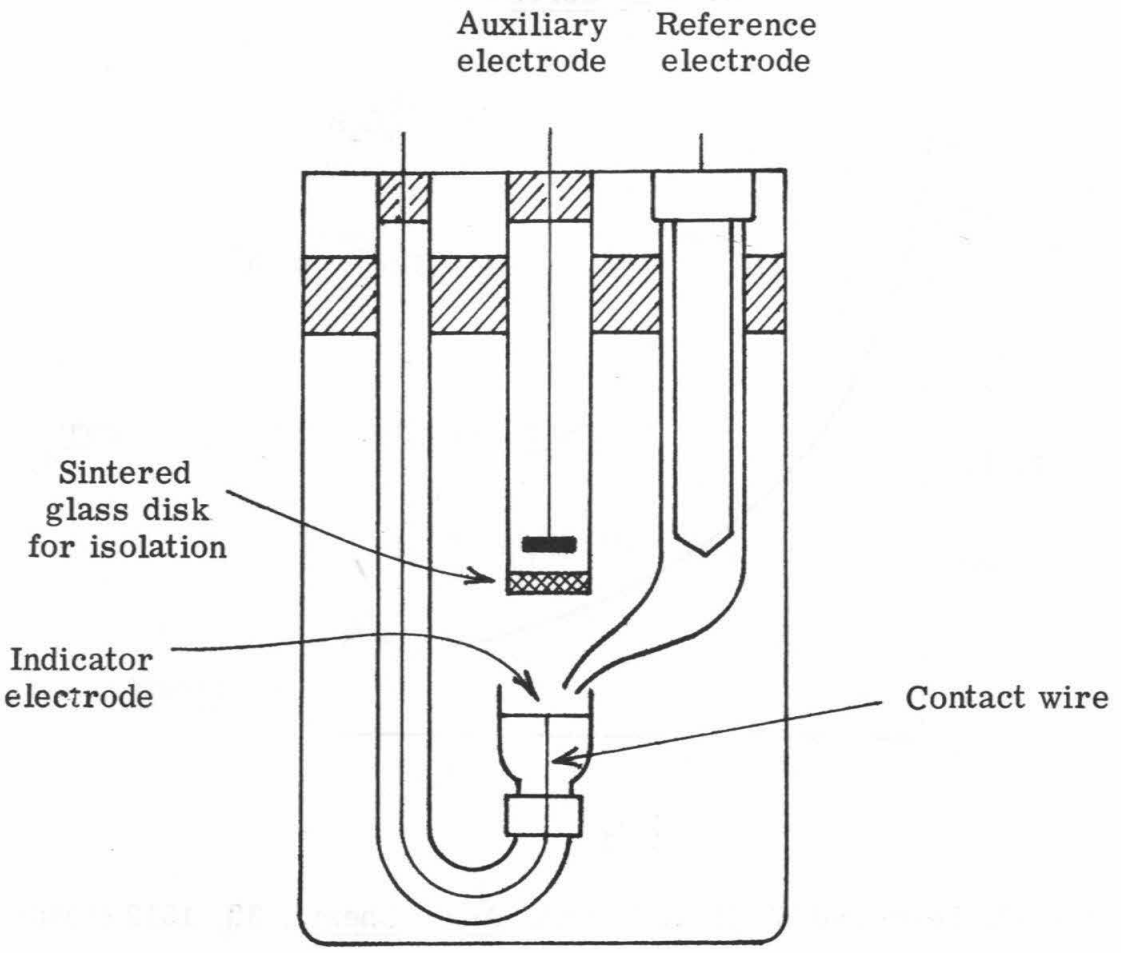
Working Curve



(E-20)

[A. C. Testa and W. H. Reinmuth, Anal. Chem., 32, 1512 (1960)]

A Typical Cell for Chronopotentiometry



(E-21)

General References on Chronopotentiometry:

1. "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Eds., Interscience Publishers Inc., New York, 1963, Part I, Vol. 4, Ch. 42, 43, 44.

2. "New Instrumental Methods in Electrochemistry," P. Delahay, Interscience Publishers Inc., New York, 1954, Ch. 8.

3. "Electroanalytical Chemistry," J. J. Lingane, Interscience Publishers, Inc., 1958, Ch. XXII.

4. D. G. Davis in "Electroanalytical Chemistry," A. J. Bard, Ed., M. Dekker, Inc., New York, 1966, Vol. 1.

5. P. J. Lingane, Critical Rev. Anal. Chem., 1, 587 (1971).

6. R. W. Murray in "Physical Methods of Chemistry, Part IIA: Electrochemical Methods," A. Weissberger and B. W. Rossiter, Eds., Wiley-Interscience, New York, 1971, Ch. VIII.

Study Problems:

1-E. A 5 millimolar solution of Cu^{2+} in 1 M H_2SO_4 is reduced to Cu under chronopotentiometric conditions giving a transition time of 25 seconds at a 2 cm^2 platinum electrode with a current of 0.92 milliamp.

a. Calculate the diffusion coefficient for the Cu^{2+} ion in 1 M H_2SO_4.

b. If the current direction were reversed after 21 seconds, how long would the reverse transition time be? (Be careful.)

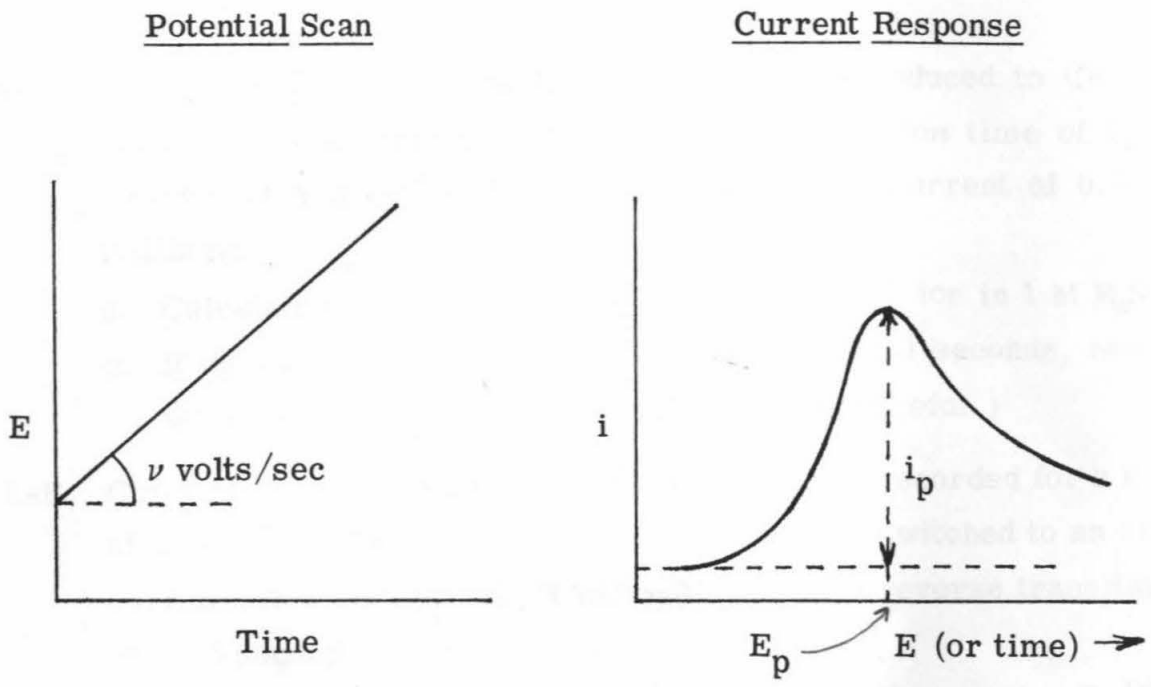
2-E. Chronopotentiogram with current reversal was recorded for a solution of $Co(en)_3^{2+}$. The initial reduction current was switched to an oxidizing current after 5.5 seconds of electrolysis and a reverse transition time of 0.95 seconds was measured.

a. Using Figure E-20 estimate the value of k_f for reaction E-19.

b. What would be the value of the reverse transition time if the forward electrolysis were reversed after 12 seconds?

Section F

Single-Sweep Voltammetry



(F-1)

$$E = E_i - \nu t \qquad \text{(F-2)}$$

initial potential

rate of potential scan

Evaluation of i_p for nernstian case:

$$Ox + n e^- \longrightarrow Red \qquad \text{(F-3)}$$

The Randles-Sevčik Equation:

At 25°C:

$$i_p = 269\, n^{3/2}\, A\, D^{1/2}\, \nu^{1/2}\, C^b \text{ (amp)} \qquad \text{(F-4)}$$

Units: $A\,(cm^2)$, $D\,(cm^2\ sec^{-1})$, ν (volts sec^{-1}), C^b (molar)

For reductions, at 25°C:

$$E_{p_C} = E^o_{ox,red} - \frac{0.029}{n}\left[1 + \log \frac{D_{ox}}{D_{red}}\right] \text{ (volt)} \qquad \text{(F-5)}$$

↑ $i_{ox.}$: +

non nernst: E_p depend on scan rate

Sensitivity:

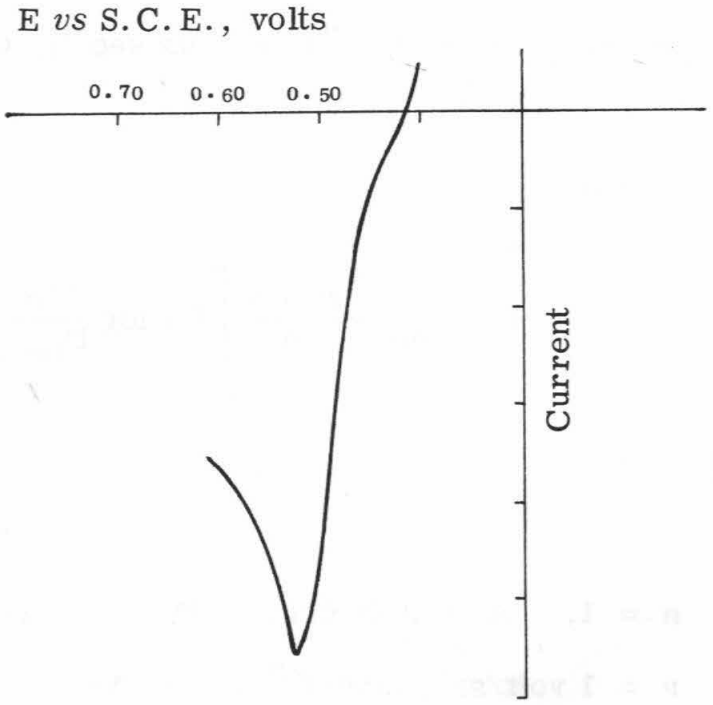
For: $n = 1$, $A = 0.01\ cm^2$, $D = 10^{-5}\ cm^2/sec$, (F-6)

$\nu = 1$ volt/sec, and $C^b = 10^{-3}$ M:

$i_p = 8.5 \times 10^{-6}$ amp $= 8.5\ \mu$amp

Analytical Application--Determination of N, N′-tetramethylbenzidine by oxidation at a Pt wire electrode:

[R. N. Adams, in "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Eds., Interscience Publishers, Inc., New York, Part I, Vol. 4, p. 2381.)



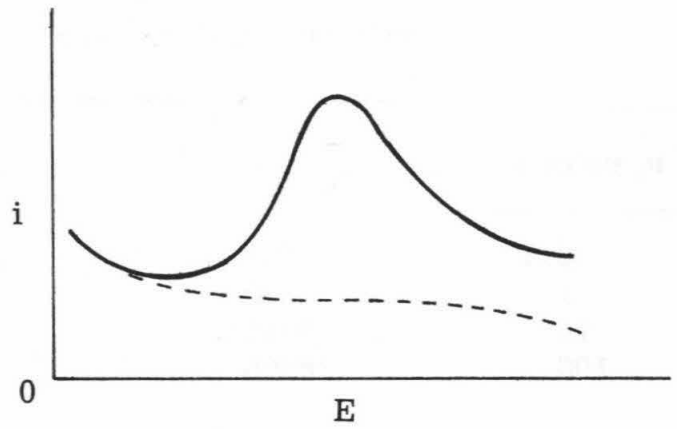
(F-7)

Calibration Date for N, N, N′, N′-Tetramethylbenzidine

Conc, M	i_p, ma	10^{-4} i_p/C (ma M^{-1})
4.0×10^{-5}	3.6	9.00
8.0×10^{-5}	7.6	9.50
1.2×10^{-4}	11.1	9.25
1.6×10^{-4}	14.2	8.87
2.0×10^{-4}	17.4	8.70
3.2×10^{-4}	26.7	8.34
4.0×10^{-4}	32.7	8.18
	Mean	8.83
	Deviation, %	4.2

(F-8)

Double Layer Charging Current:



(F-9)

Double Layer Capacitance:

$$C_{d.l.} = \frac{dq^m}{dE} = 20\text{-}80\ \mu F/cm^2 \qquad \text{(F-10)}$$

q^m = charge density on electrode

$$\frac{i_c}{A} = \frac{dq^m}{dt} = \frac{dq^m}{dE} \cdot \frac{dE}{dt} = C_{d.l.}\ \nu \qquad \text{(F-11)}$$

$$\frac{i_{c/A}}{i_{p/A}} = \frac{C_{d.l.}\ \nu}{269\ n^{3/2}\ D^{1/2}\ C^b\ \nu^{1/2}} \qquad \text{(F-12)}$$

Ratio of Charging Current to Faradaic Peak Current in Single-Sweep Voltammetry (F-13)

$n = 1$; $C_{d.l.} \simeq 25\ \mu F/cm^2$; $D = 10^{-5}\ cm^2/sec$

C^b, M	ν, volts/sec	i_p, $\mu A/cm^2$	i_c/i_p
10^{-3}	0.1	269	.009
	1	850	.029
	10	2687	.092
	100	8500	.29
10^{-5}	0.1	2.7	.9
	1	8.5	2.9
	10	26.9	9.2
	100	85.0	29

Diagnostic Applications:

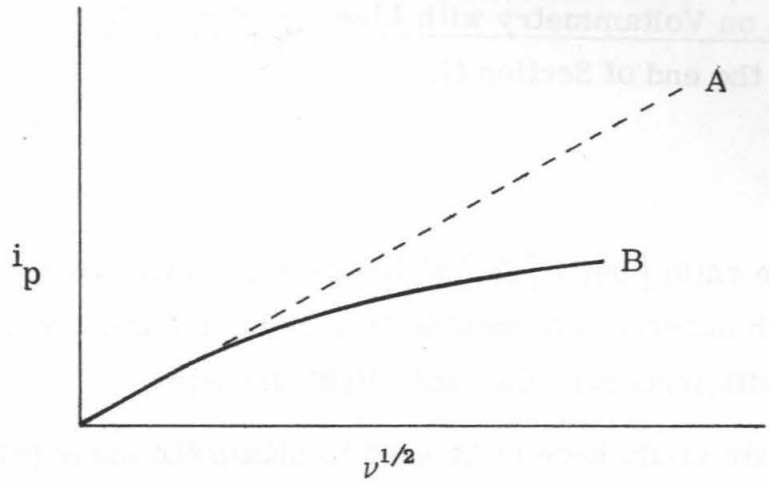
1. Detection of a chemical reaction antecedent to the electrode reaction:

Example: Nitrilotriacetate (NTA^{3-}) complexes of cadmium(II)

[M. S. Shuman and I. Shain, Anal. Chem., 41, 1818 (1969)]

$$Cd(NTA)^- + H^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Cd^{2+} + HNTA^{2-} \qquad \text{(F-14)}$$

$$Cd^{2+} + 2e^- \xrightarrow{Hg} Cd(Hg) \qquad \text{(F-15)}$$

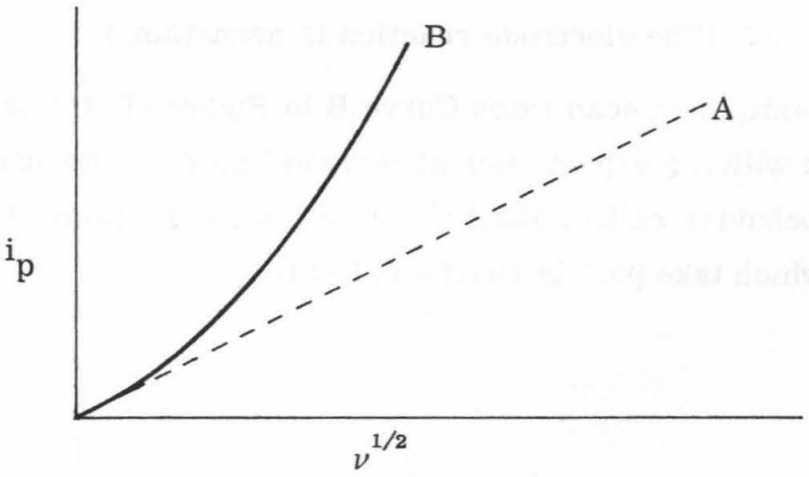


(F-16)

A -- Dissociative equilibrium (Reaction F-14) rapidly established

B -- Reaction (F-14) sluggish

2. Detection of strong adsorption of reactants



(F-17)

A -- No reactant adsorption

B -- Reactant adsorption

General References on Voltammetry with Linear Potential Scan

are given at the end of Section G.

Study Problems

1-F. Calculate the ratio [Red]/[Ox] at the peak potential for a nernstian system which undergoes a one-electron reduction and for which the diffusion coefficients for "Ox" and "Red" are equal.

2-F. What scan rate would have to be used to obtain the same peak current with a 10^{-4} M solution of Cu^{2+} as was obtained with a 3 mM solution of Tl^{+} at a scan rate of 1 volt sec^{-1}? ($D_{Tl^+} = 2 \times 10^{-5}$ cm/sec; $D_{Cu^{2+}} = 0.72 \times 10^{-5}$ cm^2 sec^{-1}; both cations exhibit nernstian behavior and are reduced to the corresponding metal amalgams.)

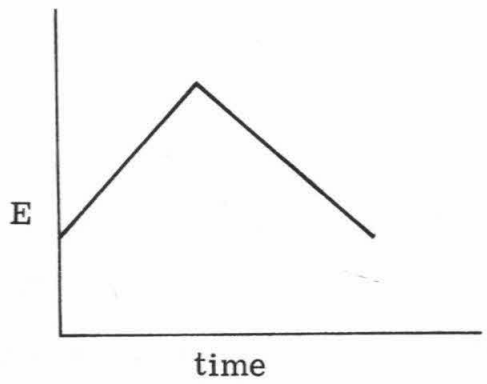
3-F. A solution of Cd^{2+} gave a peak current of 85 microamp during a single-sweep voltammetric experiments. The scan rate was 0.2 volt sec^{-1}. If the same solution and electrode were used in a chronoamperometric experiment what constant value of $it^{1/2}$ would be observed? (The electrode reaction is nernstian.)

4-F. At sufficiently high scan rates Curve B in Figure (F-16) becomes linear but with a much smaller slope than line A. What does this limiting behavior reflect about the initial concentrations of the ionic species which take part in reaction (F-14)?

Section G

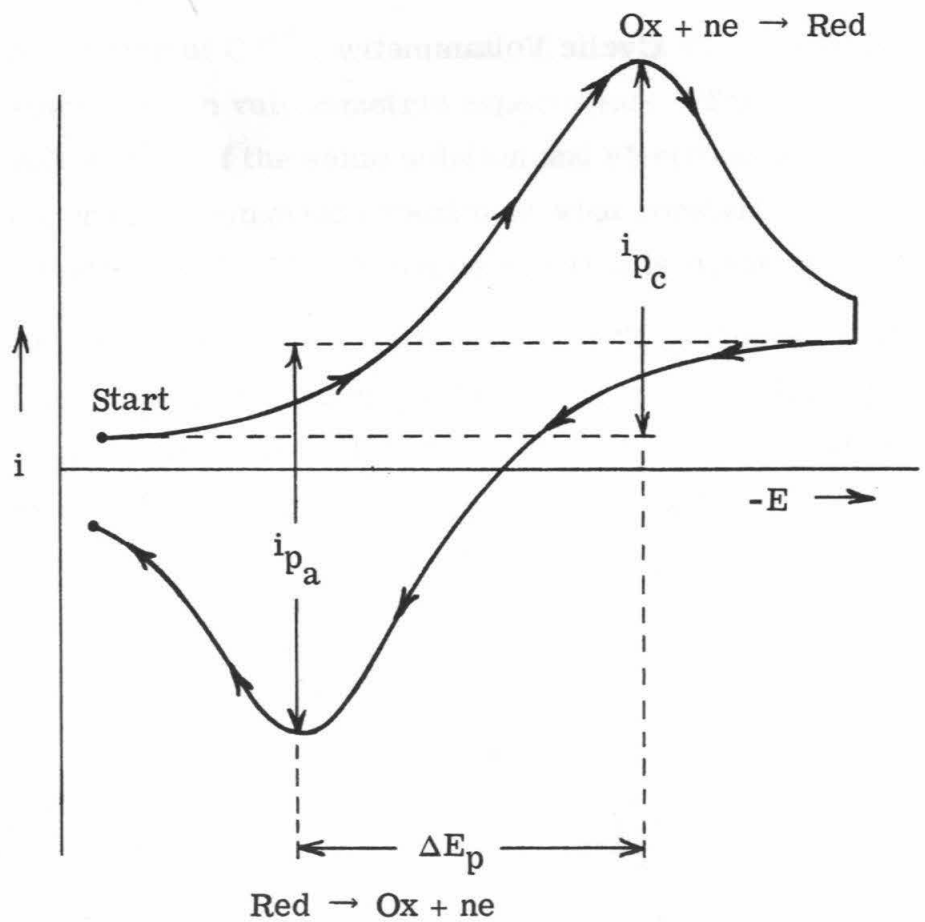
Cyclic Voltammetry

Cyclic Potential Scan



(G-1)

Current Response



(G-2)

For nernstian reactions:

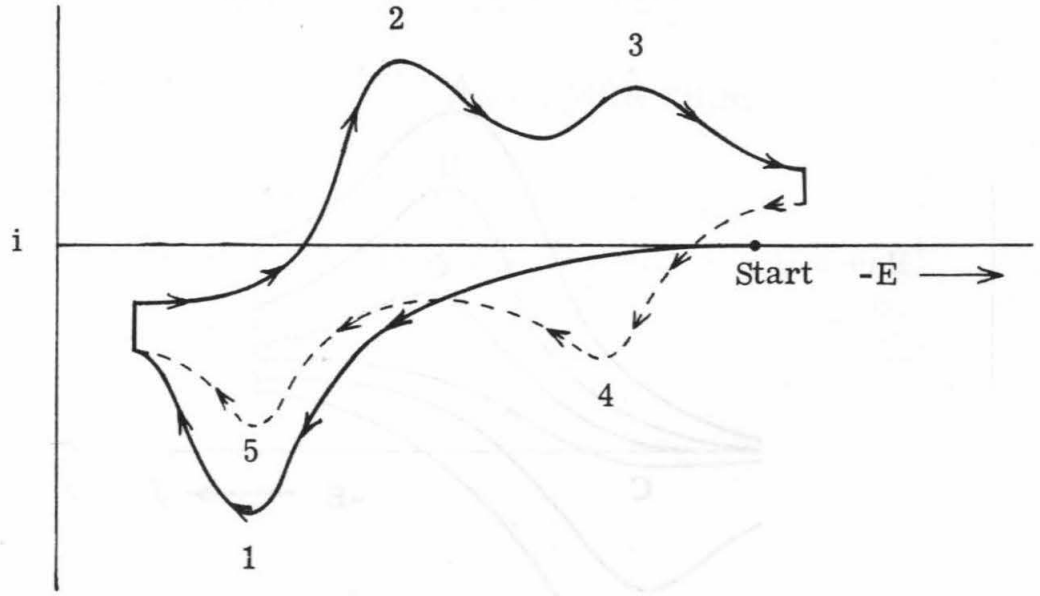
$$\Delta E_p = E_{p_a} - E_{p_c} = \frac{57-63}{n} \text{ mV at } 25^\circ \qquad \text{(G-3)}$$

$$E^0_{ox,red} = \frac{E_{p_a} + E_{p_c}}{2} + \frac{0.029}{n} \log \frac{D_{ox}}{D_{red}} \qquad \text{(G-4)}$$

$$i_{p_c} = i_{p_a} \qquad \text{(G-5)}$$

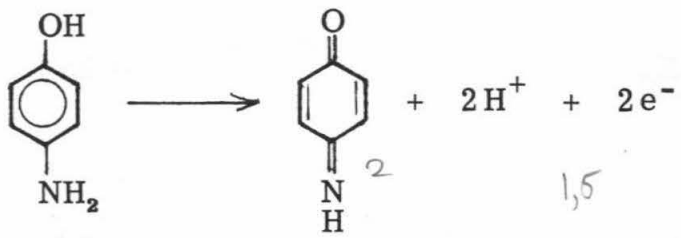
Typical Applications:

1. More than one electroactive product:

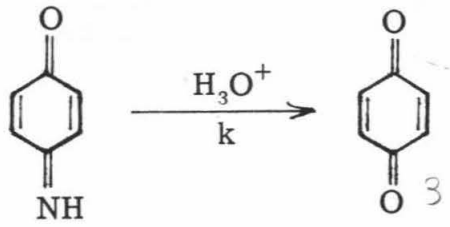


(G-6)

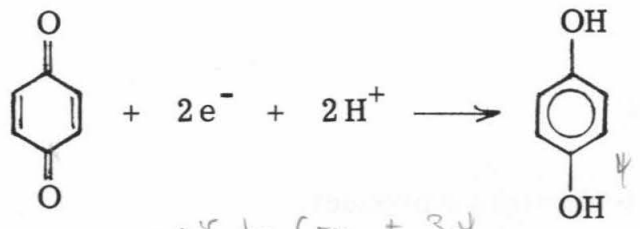
Example:



(G-7)

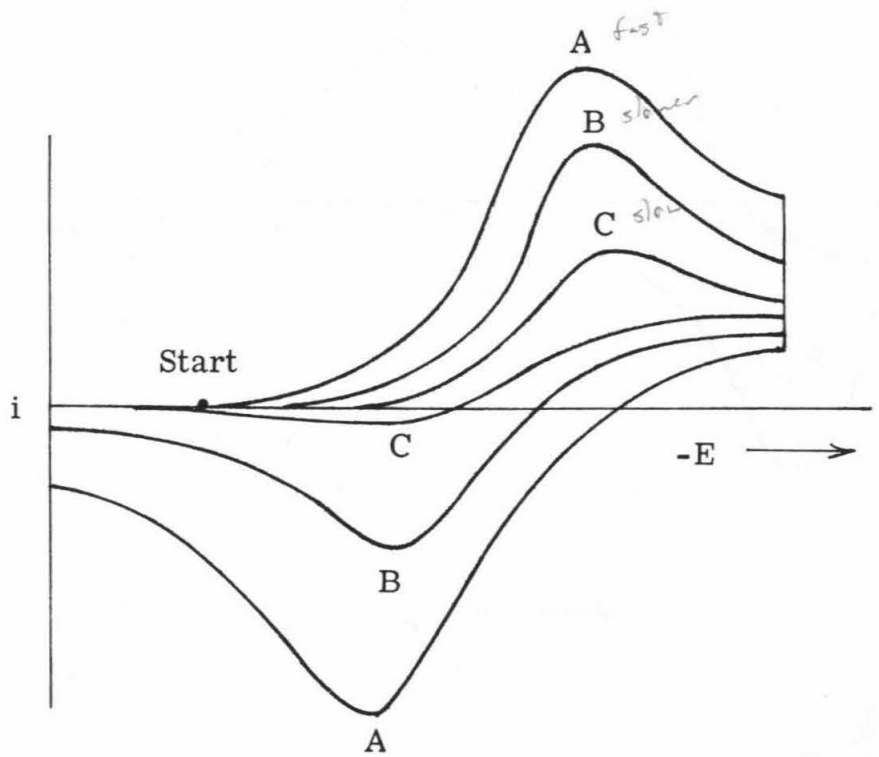


(G-8)



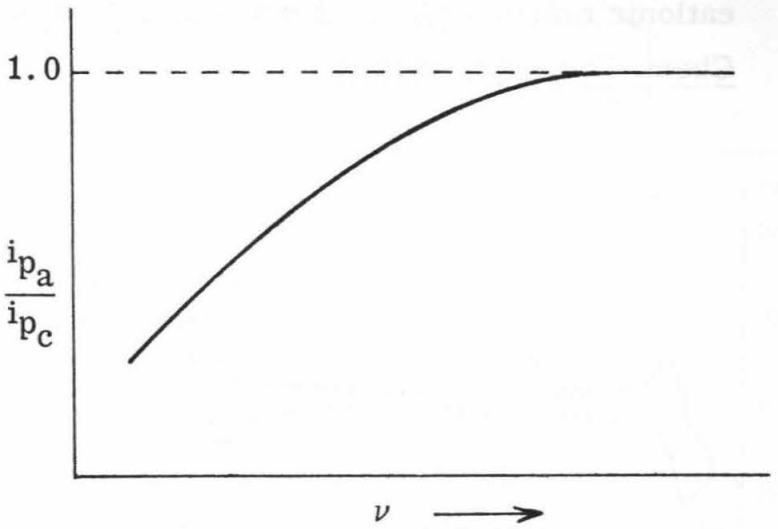
(G-9)

2. Initial electrode reaction product is converted to a non-electroactive form:



(G-10)

Effect of Loss of Product on the Peak Current Ratio



(G-11)

Example:

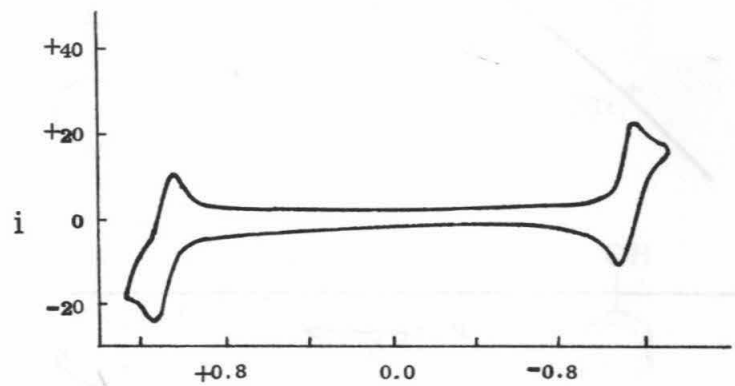
$$Co(en)_3^{3+} + e^- \rightleftharpoons Co(en)_3^{2+} \qquad \text{(G-12)}$$

(en = $H_2NCH_2CH_2NH_2$)

$$Co(en)_3^{2+} \xrightarrow[k_f]{H_3O^+} Co(en)_2^{2+}(OH_2)_2 + enH^+ \qquad \text{(G-13)}$$

3. Evaluation of standard potentials for relatively unstable systems:

Example: Electrochemical generation of anionic and cationic radicals [A. J. Bard *et al.*, J. Amer. Chem. Soc., 94, 4872 (1972)]



(G-14)

$$R^{+\cdot} \xleftarrow{-e} R \xrightarrow{+e} R^{-\cdot}$$

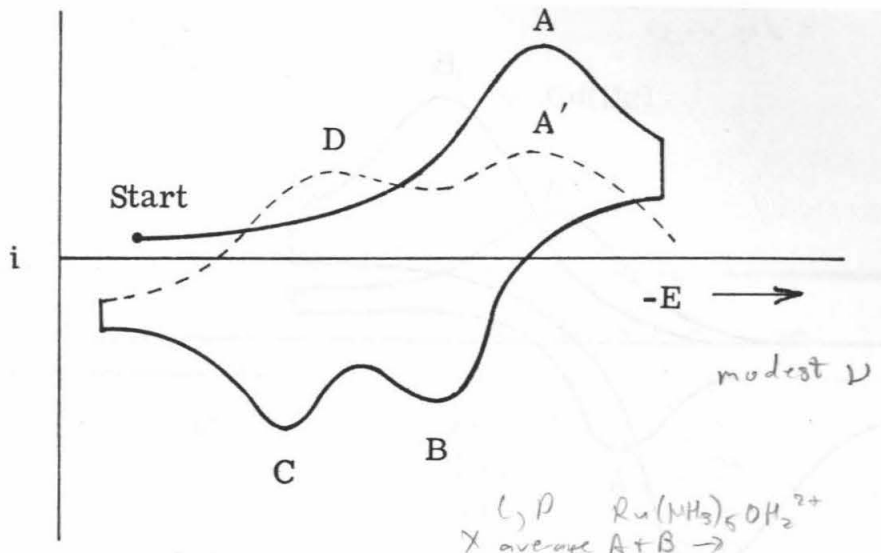
Example: Determination of E^0 for

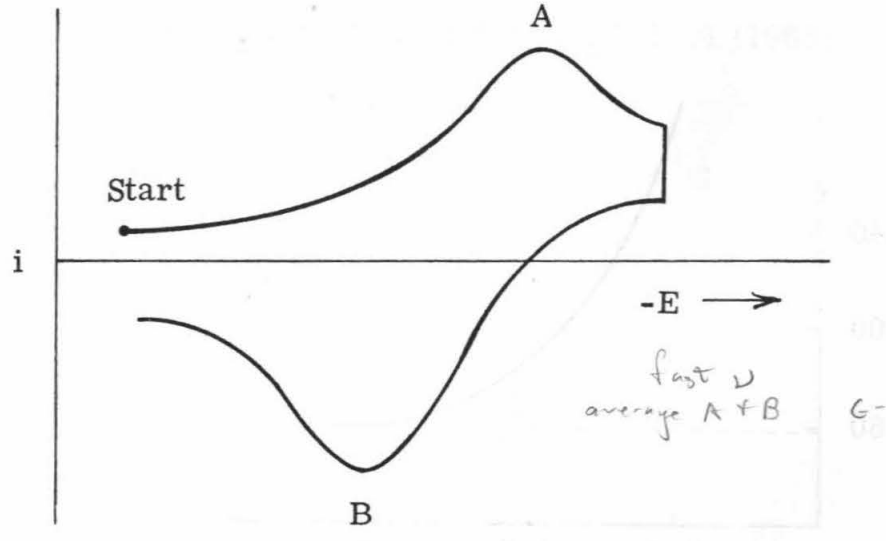
$$Ru(NH_3)_5Cl^{2+} + e \longrightarrow Ru(NH_3)_5Cl^{+} \qquad \text{(G-15)}$$

before the occurrence of

$$Ru(NH_3)_5Cl^{+} + H_2O \longrightarrow Ru(NH_3)_5OH_2^{2+} + Cl^{-} \qquad \text{(G-16)}$$

[H. S. Lim *et al.*, Inorg. Chem., 11, 1460 (1972); G. N. Coleman *et al.*, *ibid.*, 12, 1036 (1973)]



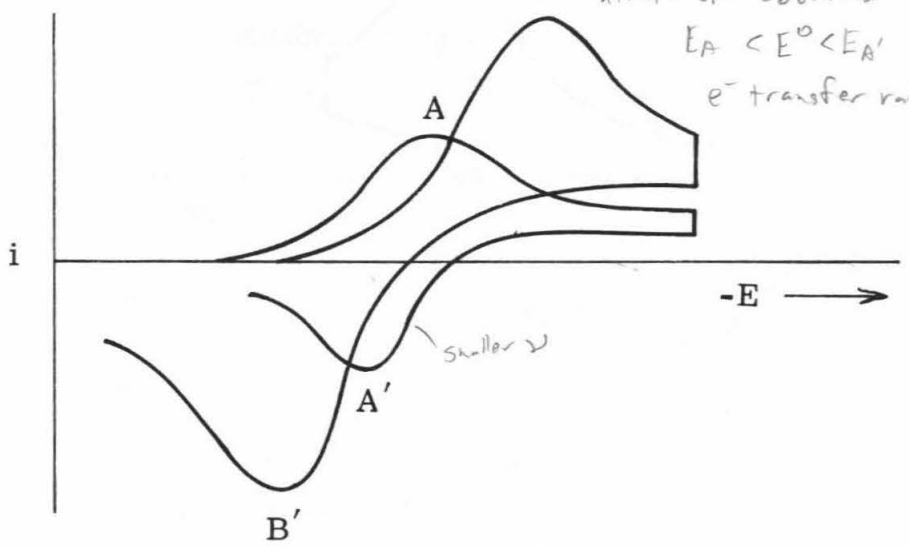


$$Ru(NH_3)_5OH_2^{2+} \longrightarrow Ru(NH_3)_5OH_2^{3+} + e^- \qquad \text{(G-19)}$$

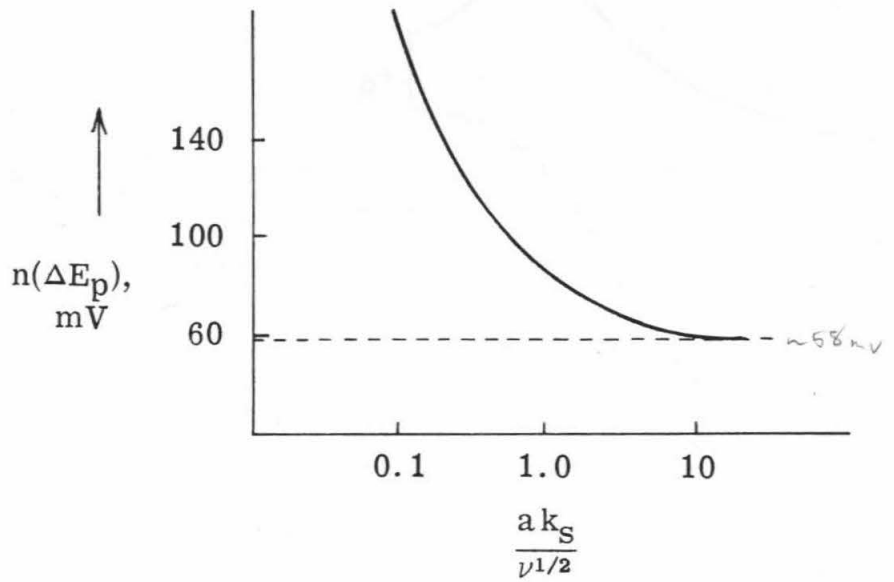
4. Detection of deviations from nernstian behavior:

G-4: nernst
x dep on ν

if is → non nernst
limits still obtained
$E_A < E^\circ < E_{A'}$
e^- transfer rate limiting



(G-20)



(G-21)

[R. S. Nicholson, Anal. Chem., 37, 1351 (1965)]

$$a \sim \left(\frac{RT}{\pi n F D_{ox}}\right)^{1/2} \qquad \text{(G-22)}$$

Example:

$$Cd^{2+} + 2e^- \xrightarrow{Hg} Cd(Hg) \qquad \text{(G-23)}$$

ν, volts/sec	$2\Delta E_p$, mV	k_s, cm/sec
48	94	0.25
60	98	0.25
90	108	0.24
120	115	0.23

(G-24)

[R. S. Nicholson, Anal. Chem., 37, 1351 (1965)]

ohmic R → non nernstian too

General References on Linear Potential Scan and Cyclic Voltammetry:

1. A series of papers by R. S. Nicholson, I. Shain, and co-workers: Anal. Chem., 36, 706 (1964); 37, 178, 190, 1351 (1965); 38, 150, 370, 376, 1406 (1966); 39, 1514, 1527, 1535 (1967); 41, 1818 (1969); 42, 162 (1970); 44, 1647, 1786 (1972). (See also the series of papers by J. M. Saveant and co-workers in J. Electroanal. Chem., 1970-1974, for detailed discussions of more complex applications.)

2. Chapter 5 in R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, Inc., New York, 1969.

3. "A Guide to the Study of Electrode Kinetics," H. R. Thirsk and J. A. Harrison, Academic Press, New York, 1972, Chapter 2.

4. E. R. Brown and R. F. Large in "Physical Methods of Chemistry, Part IIA: Electrochemical Methods," A. Weissberger and B. W. Rossiter, Eds., Wiley-Interscience, New York, 1971, Ch. VI.

Study Problems:

1-G. In sulfuric acid solutions cyclic voltammograms for Cu^{2+} at a mercury electrode contain a reduction and an oxidation wave that have peak potentials separated by 29 mV. However, in hydrochloric acid solutions of Cu^{2+} a pair of reduction-oxidation waves are obtained and each set has a ΔE_p of 59 mV. Propose an explanation for this difference in behavior.

2-G. The peak potentials in Figure G-14 are as follows: E_{p_c} = -1160 and +1060 mV; E_{p_a} = -1100 and +1120 mV.

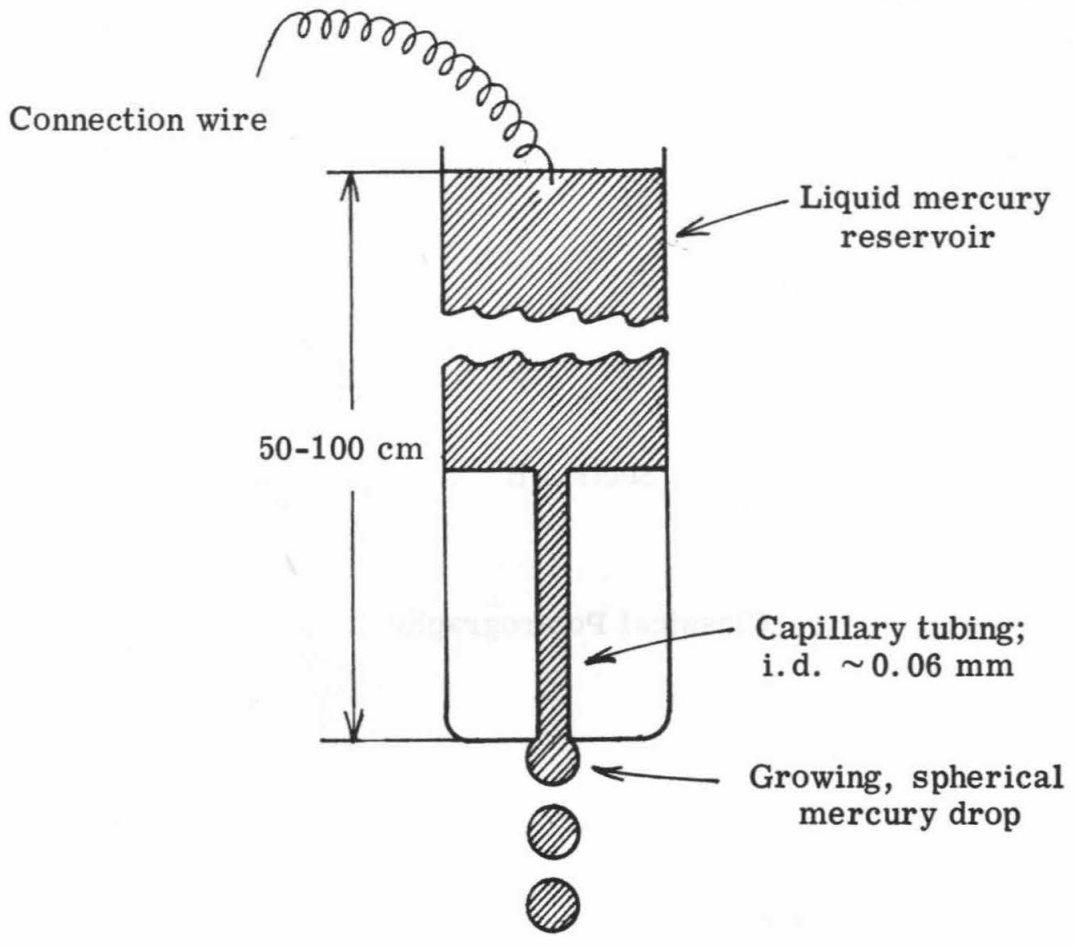
a. Evaluate approximate standard potentials for the half-reactions $R + e^- \rightarrow R^{-}\cdot$ and $R \rightarrow R^{+}\cdot + e^-$.

b. Calculate the free energy released by the reaction between $R^{-}\cdot$ and $R^{+}\cdot$.

Section H

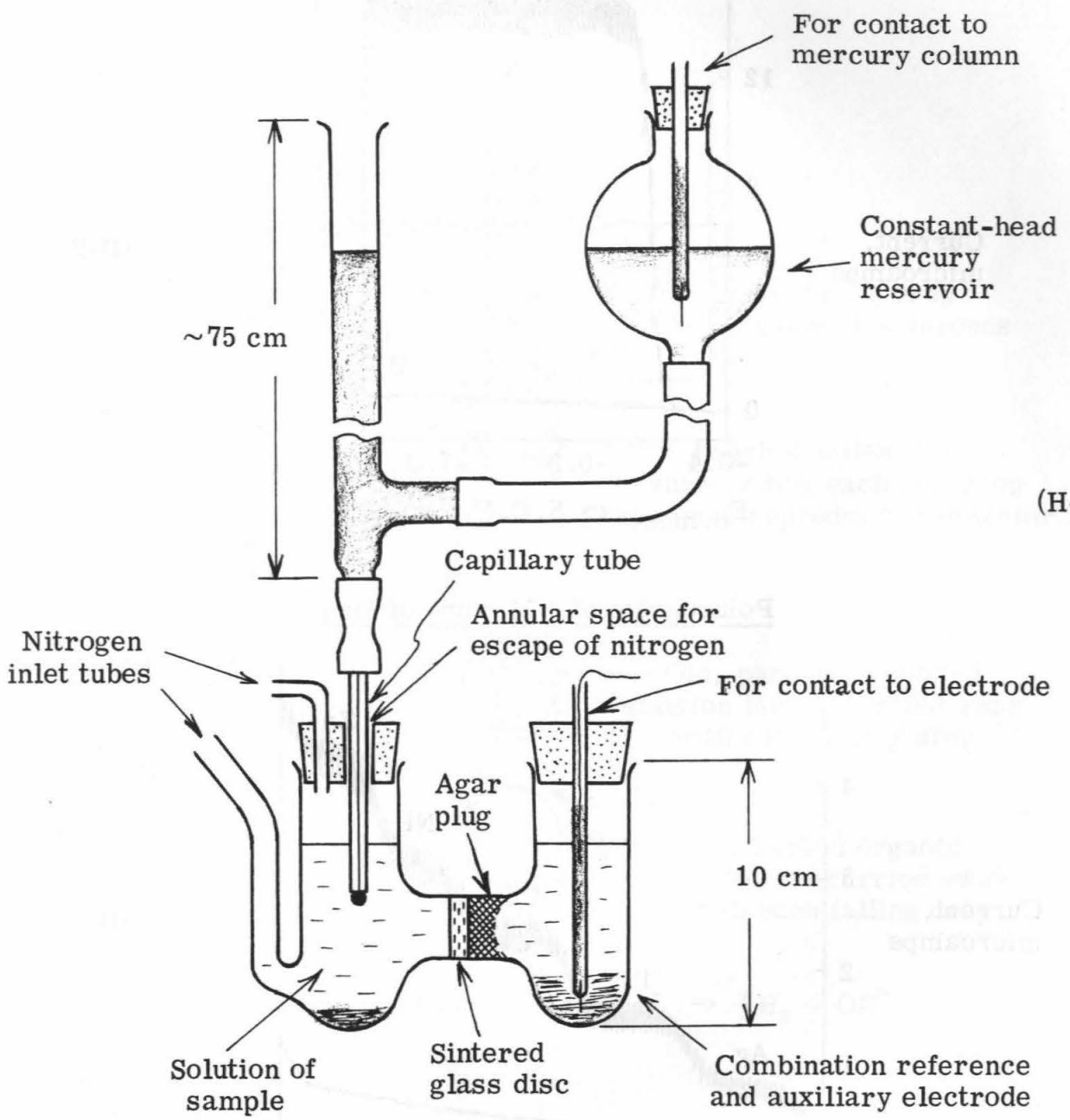
Classical Polarography

Dropping Mercury Electrode (D.M.E.)



(H-1)

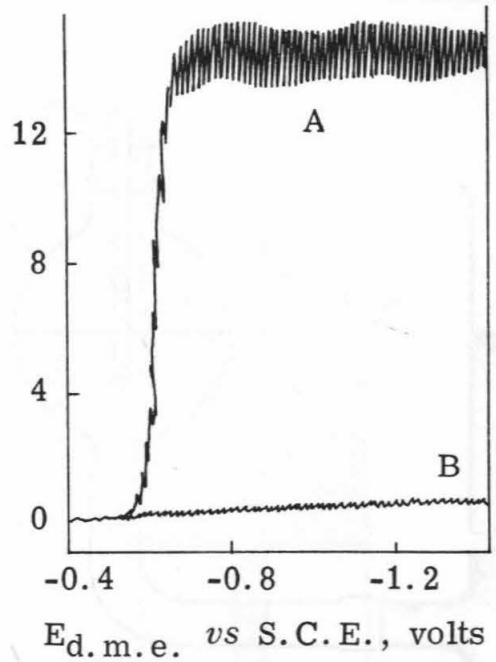
A Two-Electrode Polarographic Cell



(H-2)

[J. J. Lingane and H. A. Laitinen, Anal. Chem., 11, 504 (1939)]

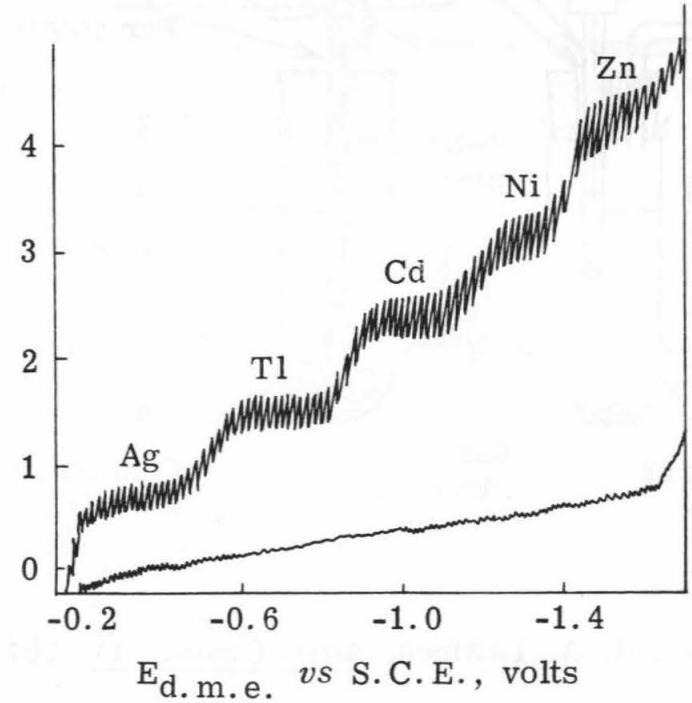
Typical Polarogram



Current, microamps

(H-3)

Polarogram of a Mixture of Ions



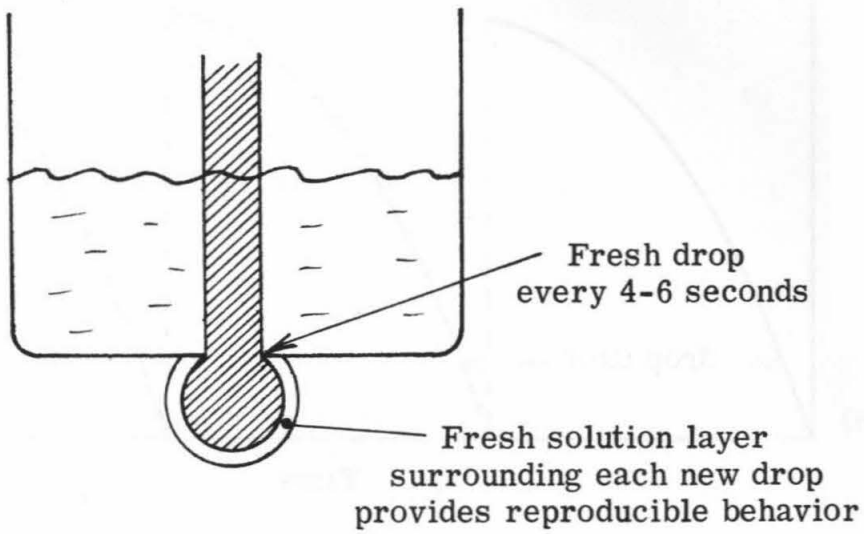
Current, microamps

(H-4)

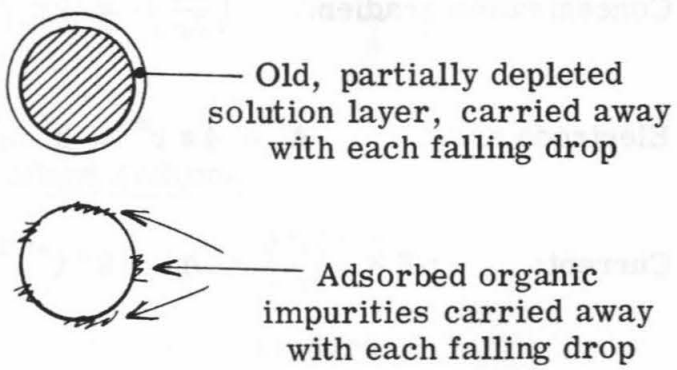
[Adapted from L. Meites, "Polarographic Techniques," Interscience Publishers, New York, 1965]

Virtues of the Dropping Mercury Electrode (H-5)

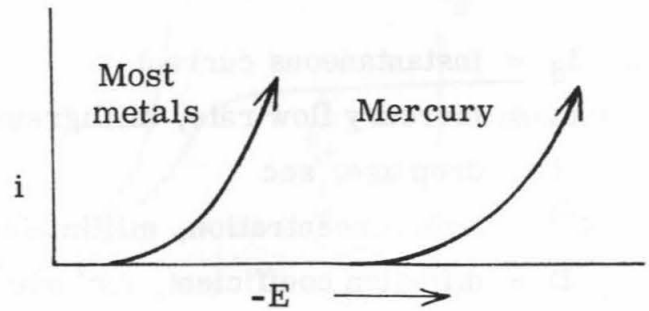
1. Reproducibility:



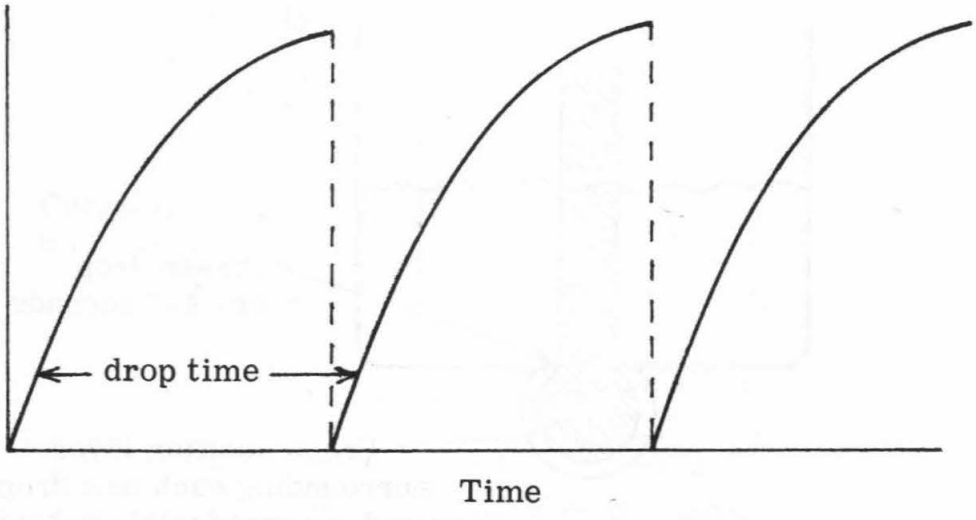
2. Self-cleansing:



3. High "hydrogen overvoltage": $H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$



Instantaneous Current-time Curves for a Dropping Mercury Electrode



etc. (H-6)

Concentration gradient: $\left(\frac{\partial C}{\partial r}\right) = k t^{-1/2}$ (H-7)

Electrode area: $A = 4\pi r^2 = k' m^{2/3} t^{2/3}$ (H-8)

Current: $nF \times \left(\frac{\partial C}{\partial r}\right) \times A = k'' t^{-1/2 + 2/3 = 1/6}$ (H-9)

The Ilkovič Equation:

$$i_d(\mu amp) = 708\, n D^{1/2} C^b m^{2/3} t^{1/6} \quad \text{(H-10)}$$

i_d = instantaneous current
m = mercury flow rate, milligrams/sec
t = drop age, sec
C^b = bulk concentration, millimolar
D = diffusion coefficient, $cm^2\ sec^{-1}$

$$i_d(\text{avg.}) = 607\, n\, D^{1/2}\, C^b\, m^{2/3}\, t_d^{1/6} \qquad \text{(H-11)}$$

t_d = drop life, *i.e.*, t at drop fall

Quantitative Polarographic Analysis:

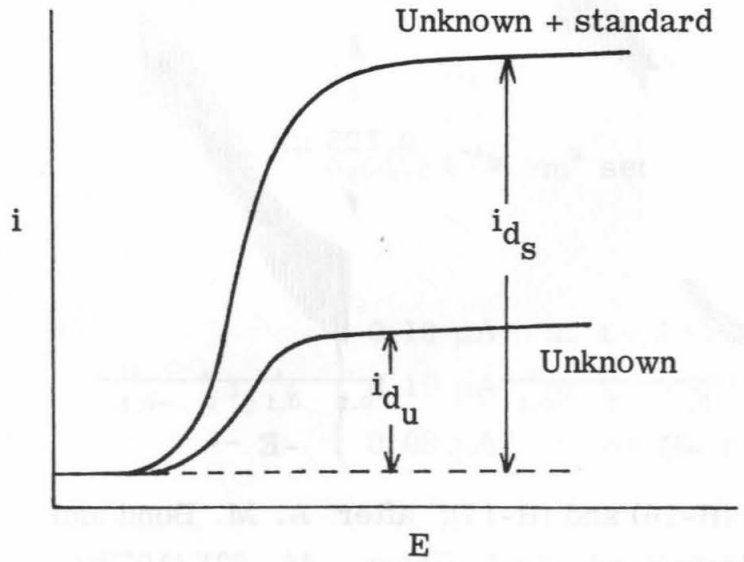
Diffusion Current Constant

$$I \equiv 708\, n\, D^{1/2} \qquad \text{(H-12)}$$

$$C^b = \frac{i_d}{I\, m^{2/3}\, t^{1/6}} \qquad \text{(H-13)}$$

i) Measure: i_d, m and t
ii) Look up (or measure): I
iii) Calculate: C^b

Standard Addition



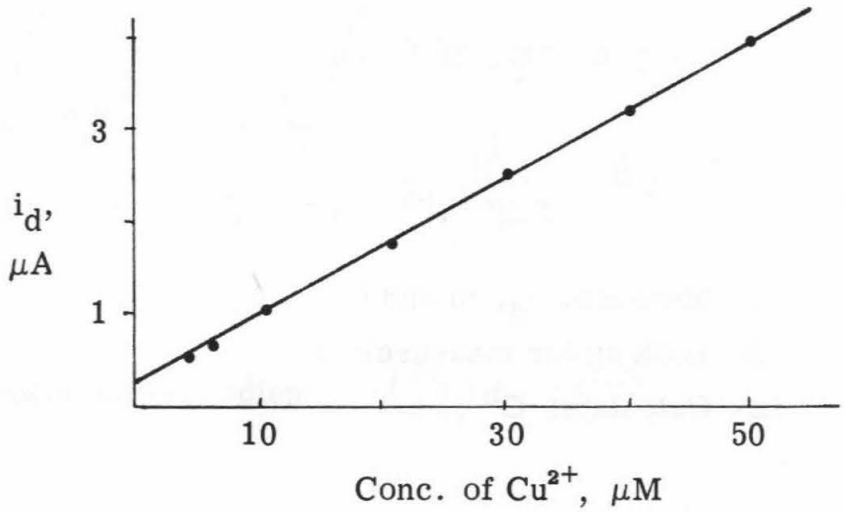
(H-14)

$$C_u = \frac{C_s V_s (i_d)_u}{(V_u + V_s)(i_d)_s - V_u (i_d)_u} \qquad \text{(H-15)}$$

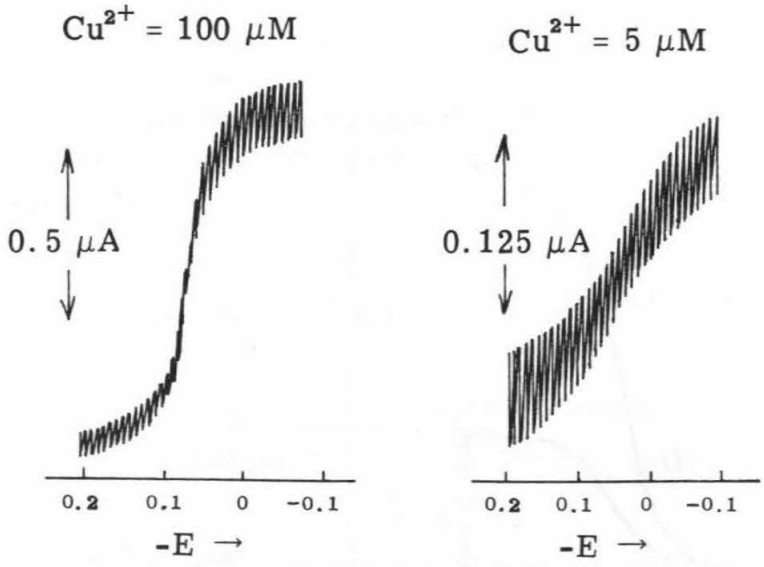
C_s, C_u, V_s, V_u = Concentrations and Volumes of standard and unknown solutions

best: $V_u \rightarrow i_d$ ↑×2

Calibration Curves



(H-16)



(H-17)

[Figures (H-16) and (H-17); after A. M. Bond and D. R. Canterford, Anal. Chem., 44, 721 (1972)]

Typical values of parameters involved in Ilkovič equation:

$n = 2$ electrons; $D = 10^{-5}$ cm^2 sec^{-1};
$m = 2$ mg sec^{-1}; $t_d = 4$ sec

$$i_d = 8.9\, C^b\ \mu A\ (C^b \text{ in mM}) \tag{H-18}$$

C^b, mM	i_d, microamp
1	8.9
10^{-3}	8.9×10^{-3}
10^{-6}	8.9×10^{-6}

(H-19)

Limits on Sensitivity:

1. Irreducible background charging current

$$i_c = C_{d.l.} \frac{dA}{dt} (E - E_Z) \tag{H-20}$$

Typical values

$$|E - E_Z| = 0.7 \text{ volt}$$

$$C_{d.l.} = 25\ \mu F\ cm^{-2}$$

$$\frac{dA}{dt} = 0.0072\, t^{-1/3}\ cm^2\ sec^{-1}$$

$$i_c = \begin{cases} 0.13\ \mu A & \text{at } t = 1 \text{ sec} \\ 0.10\ \mu A & \text{at } t = 2 \text{ sec} \\ 0.08\ \mu A & \text{at } t = 4 \text{ sec} \end{cases} \tag{H-21}$$

2. Residual electroactive impurities--chiefly O_2

	Approx. conc of O_2 at 25°C	i_d ($O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$)
Air-saturated H_2O	0.25 mM	5 μA
Air-saturated H_2O after deaeration with N_2 for several minutes	~0.0005 mM	~0.01 μA

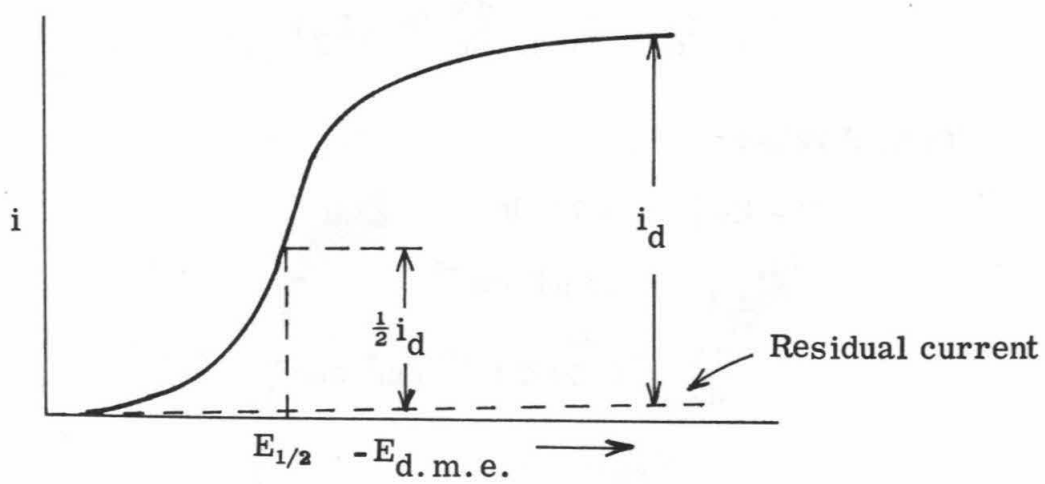
(H-22)

The Shape of Polarographic Waves

For nernstian systems:

$$E_{d.m.e.} = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \qquad \text{(H-23)}$$

(cf. Section A)

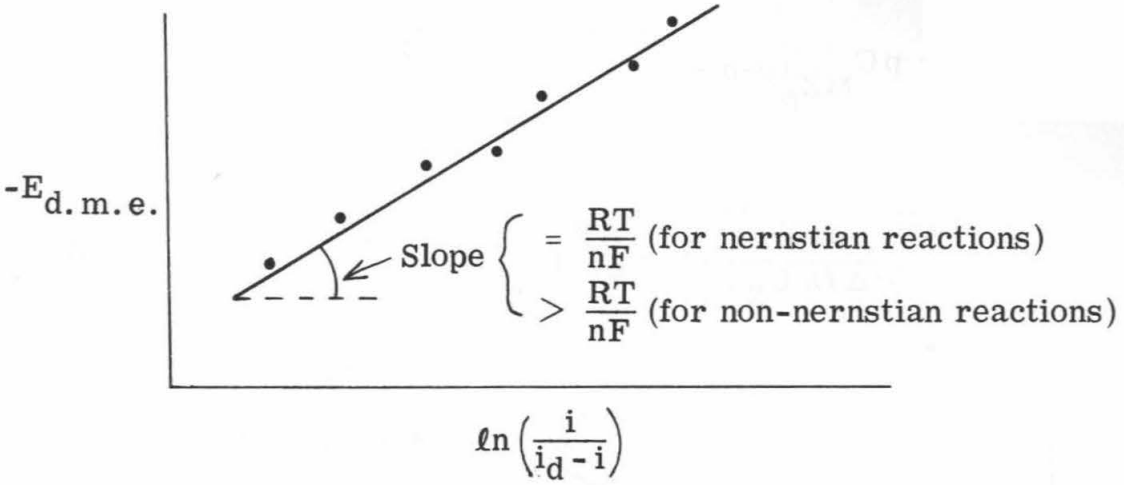


(H-24)

Parameters characterizing a typical polarogram (shown without current fluctuations)

$$E_{1/2} = E^0_{ox, red} - \frac{RT}{2nF} \ln \left(\frac{D_{ox}}{D_{red}} \right) \qquad \text{(H-25)}$$

Graphical Analysis of Wave Shapes



(H-26)

Polarography of metal ion complexes:

$$M^{n+} + pX^- \rightleftharpoons MX_p^{(p-n)-}; \quad K_{MX_p} \tag{H-27}$$

$$MX_p^{(p-n)-} + ne^- \longrightarrow M(Hg) + pX^- \tag{H-28}$$

$$E_{d.m.e.} = E_{1/2} - \frac{RT}{nF} \ell n \frac{i}{i_d - i} \tag{H-29}$$

but

$$E_{1/2} = E^0_{M^{n+}, M(Hg)} - \frac{RT}{2nF} \ell n \frac{D_{MX_p}}{D_{M(Hg)}} - \frac{RT}{nF} \ell n K_{MX_p} - \frac{RT}{nF} p \ell n (C_{X^-}) \tag{H-30}$$

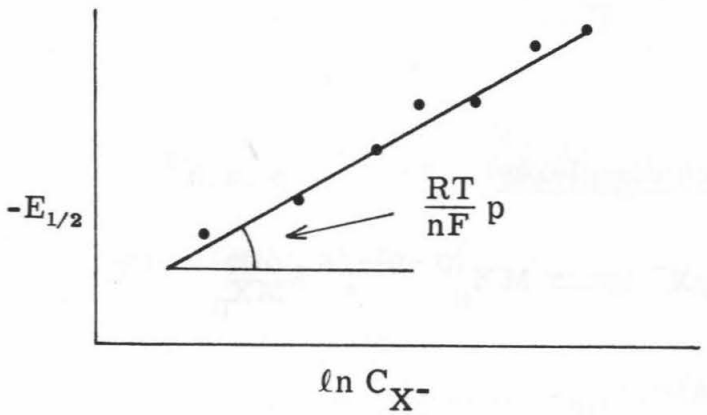
$$\left(\text{Valid for nernstian reactions when } p C_{MX_p^{(p-n)-}} \gg C_{M^{n+}} \right)$$

Properties of the Half-Wave Potential for Complex Ions:

1. Evaluation of p

when $C_{X^-} \gg p C_{MX_p^{(p-n)-}}$

$$\frac{\Delta E_{1/2}}{\Delta \ell n\, C_{X^-}} = -\frac{RT}{nF} p \qquad \text{(H-31)}$$



(H-32)

Example:

$$Cd(en)_p^{2+} + 2e^- \xrightarrow{Hg} Cd(Hg) + p(en) \qquad \text{(H-33)}$$

Plot of $-E_{1/2}$ *vs* $\ell n\,[en]$ has a slope $= \frac{1.5\,RT}{F}$;

$\therefore$ since $n = 2$, $p = 3$

2. Evaluation of K_{MX_p}

For $$M^{n+} + ne^- \xrightarrow{Hg} M(Hg) \qquad \text{(H-34)}$$

$$E_{1/2} = E^0_{M^{n+}, M(Hg)} - \frac{RT}{2nF} \ell n \frac{D_{M(Hg)}}{D_{M^{n+}}} \qquad \text{(H-35)}$$

$E_{1/2}$ (for MX_p) - $E_{1/2}$ (for M^{n+}) = $\Delta E_{1/2}$ =

$$\frac{RT}{2nF} \ell n \left(\frac{D_{M^{n+}}}{D_{MX_p}}\right) - \frac{RT}{nF} p \ \ell n \ C_X - \frac{RT}{nF} \ell n \ K_{MX_p} \qquad \text{(H-36)}$$

$$\left(\frac{D_{M^{n+}}}{D_{MX_p}}\right)^{1/2} = \frac{(i_d)_{M^{n+}}}{(i_d)_{MX_p}} \qquad \text{(H-37)}$$

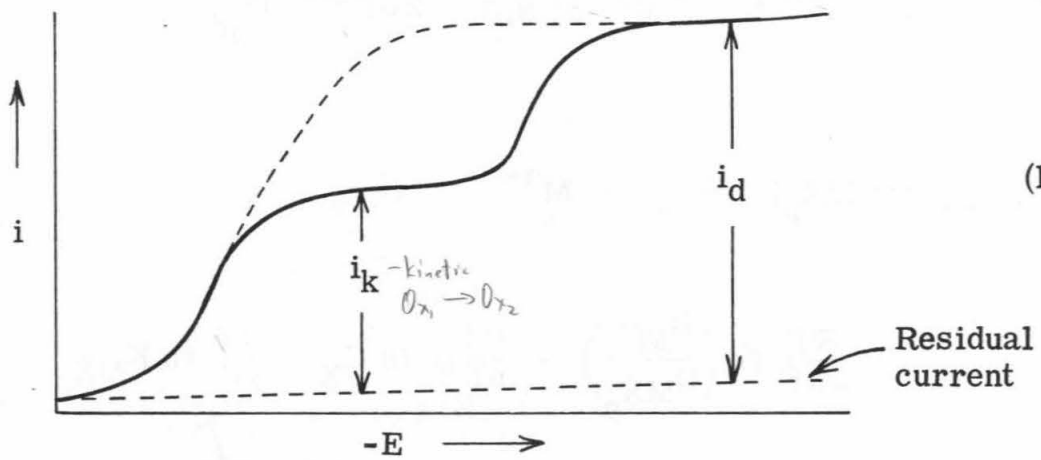
$$p \Longrightarrow \frac{\Delta E_{1/2}}{\Delta \ \ell n \ C_{X^-}} \qquad \text{(H-38)}$$

$$\Delta E_{1/2} \Longrightarrow K_{MX_p} \qquad \text{(H-39)}$$

Kinetic Currents in Polarography:

$$Ox_1 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ox_2 \qquad \text{(H-40)}$$

$$Ox_2 + ne \longrightarrow Red \qquad \text{(H-41)}$$



(H-42)

Examples:

Recombination of protons with keto-acid anions

$$CH_3\overset{\overset{O}{\|}}{C}COO^- + H^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CH_3\overset{\overset{O}{\|}}{C}COOH \text{ (pyruvic acid)} \qquad \text{(H-43)}$$

Dissociation of metal complexes

$$Cd(CN)_4^{2-} \overset{\text{fast}}{\rightleftharpoons} Cd(CN)_3^- + CN^- \qquad \text{(H-44)}$$

$$Cd(CN)_3^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Cd(CN)_2 + CN^- \qquad \text{(H-45)}$$

Dehydration of aldehydes

$$RHC(OH)_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} RH{-}C{=}O + H_2O \qquad \text{(H-46)}$$

in H_2O
X reducible

reducible

Properties of Kinetic *vs* Diffusion Currents:

$$m = k_1 h \qquad \text{(H-47)}$$

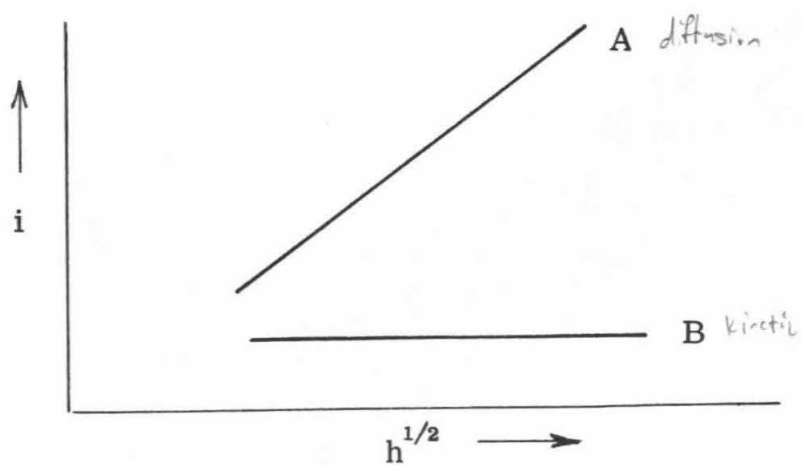
$$m t_d = \text{drop weight} = \text{constant} \qquad \text{(H-48)}$$

$$i_d = k_2 m^{2/3} t_d^{1/6} = k_2 m^{1/2} (m t_d)^{1/6} \qquad \text{(H-49)}$$

$$\therefore i_d = k_3 h^{1/2} \qquad \text{(H-50)}$$

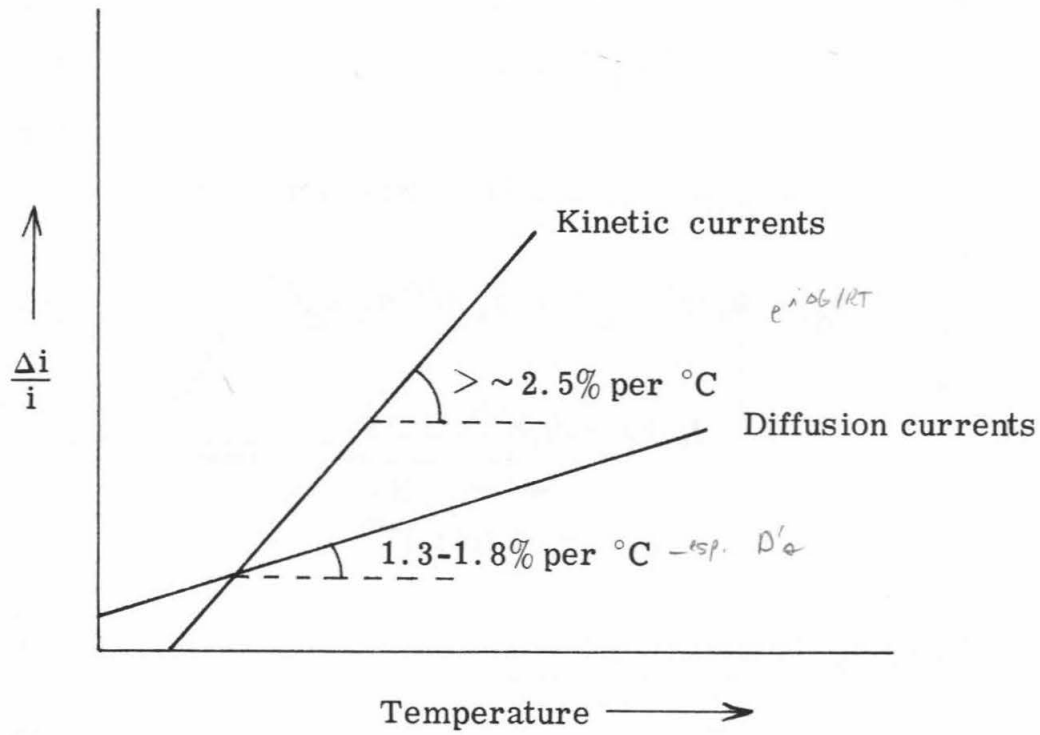
$$i_k = k_4 A = k_5 (m t_d)^{2/3} \qquad \text{(H-51)}$$

Thus, i_k is independent of h



(H-52)

Temperature Dependences of Kinetic *vs* Diffusion Currents



(H-53)

General References on Polarography:

1. "Polarography," I. M. Kolthoff and J. J. Lingane, Interscience Publishers, New York, 1952.

2. "Polarographic Techniques," L. Meites, Interscience Publishers, New York, 1965.

3. "Principles of Polarography," J. Heyrovsky and J. Kuta, Academic Press, New York, 1966.

4. L. Meites in "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Eds., Interscience Publishers, New York, 1963, Part 1, Vol. 4.

5. O. H. Müller in "Physical Methods of Chemistry, Part IIA: Electrochemical Methods," A. Weissberger and B. W. Rossiter, Eds., Wiley-Interscience, New York, 1971, Ch. V.

Study Problems

1-H. Why does the current undergo oscillations during the recording of a d.c. polarogram?

2-H. What causes finite residual currents to flow at dropping mercury electrodes in the absence of any added electroactive substances?

3-H. a. Calculate the diffusion current at a d.m.e. for a 0.001 M solution of Pb^{2+} if the mercury flow rate is 2.5 mg/sec, the drop time is 3 sec and $D_{Pb^{2+}} = 1 \times 10^{-5}$ cm^2/sec.

b. What is the current density at the electrode just before drop fall? (The density of mercury is 13.6 gr/cm^3)

c. Does the current density change during drop growth? In what way?

d. What will the current density be when a drop is 2 seconds old?

4-H. The concentration of zinc in a sample of seawater was determined polarographically by the method of standard addition. The diffusion current measured in a 25.0 ml sample of seawater was 0.14 μA. After addition of 1.00 ml of a 2×10^{-4} M solution of zinc to the seawater sample the measured diffusion current for zinc reduction was 0.32 μA. Calculate the concentration of zinc in the original sample.

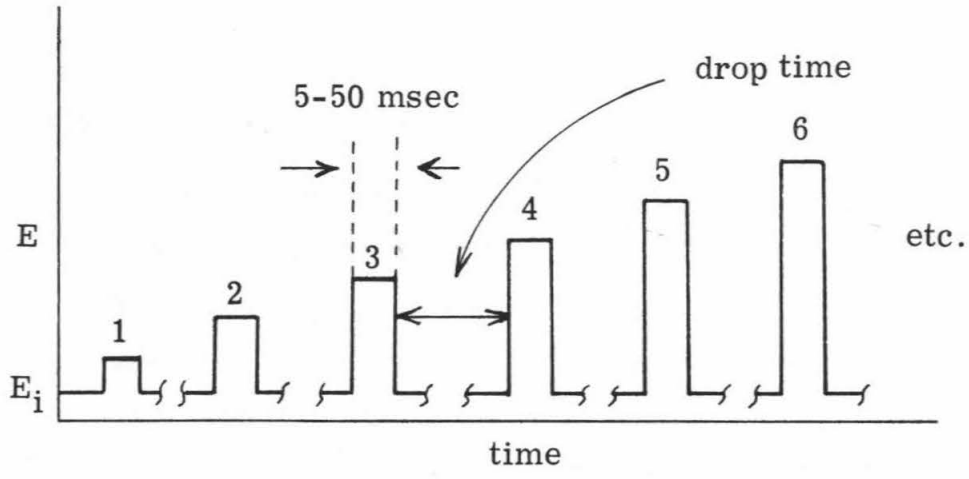
5-H. A plot of $E_{d.m.e.}$ *vs* $\ell n\left(\frac{i}{i_d - i}\right)$ for a d.c. polarogram of Cd(II) in a 1 M NH_3 electrolyte has a slope of 12.8 mV. A plot of $E_{1/2}$ *vs* $\ell n\,[NH_3]$ has a slope of 51.2 mV for $[NH_3]$ between 0.1 and 1 M. What is the predominating cadmium-ammonia complex present in these solutions?

6-H. $E_{1/2}$ for Cd^{2+} in a non-complexing electrolyte is -578 mV. In 1 M NH_3 $E_{1/2}$ is shifted to -784 mV. Calculate the formation constant for the predominate Cd(II)-ammonia complex present. (Assume equal diffusion coefficients for cadmium in both the complexed and uncomplexed forms.)

Section J

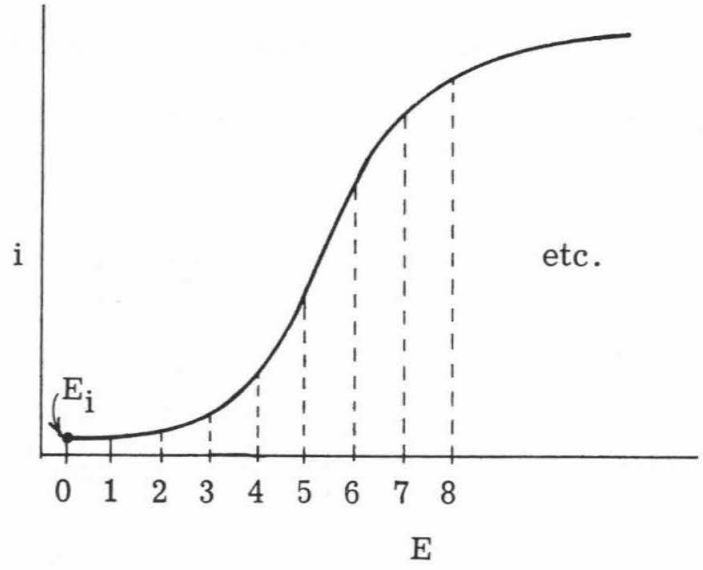
Pulse Polarography and Alternating Current Polarography

Normal Pulse Polarography



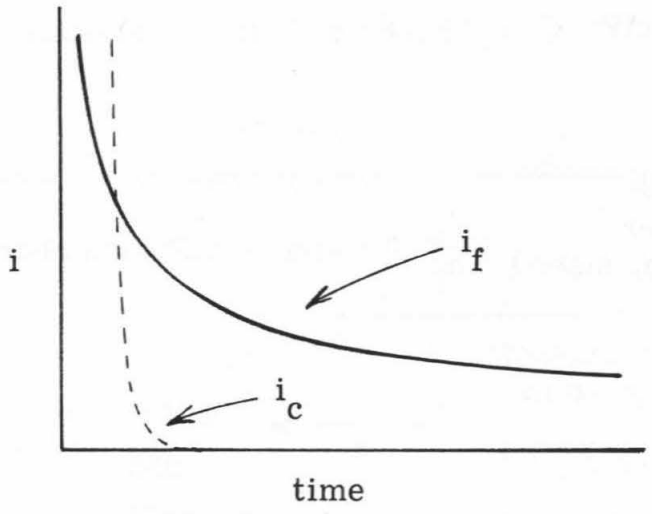
(J-1)

Current Sampling in Normal Pulse Polarography



(J-2)

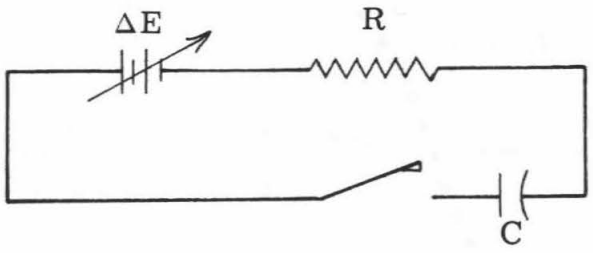
Decay of Faradaic and Charging Currents in Pulse Polarography



(J-3)

Faradaic current: $$i_f = \frac{n F A D^{1/2} C^b}{(\pi t)^{1/2}} \qquad \text{(J-4)}$$

Charging current: $$i_c = \frac{\Delta E}{R} e^{-t/RC} \qquad \text{(J-5)}$$



(J-6)

Equivalent circuit model for the electrode/electrolyte interface in the absence of reactant

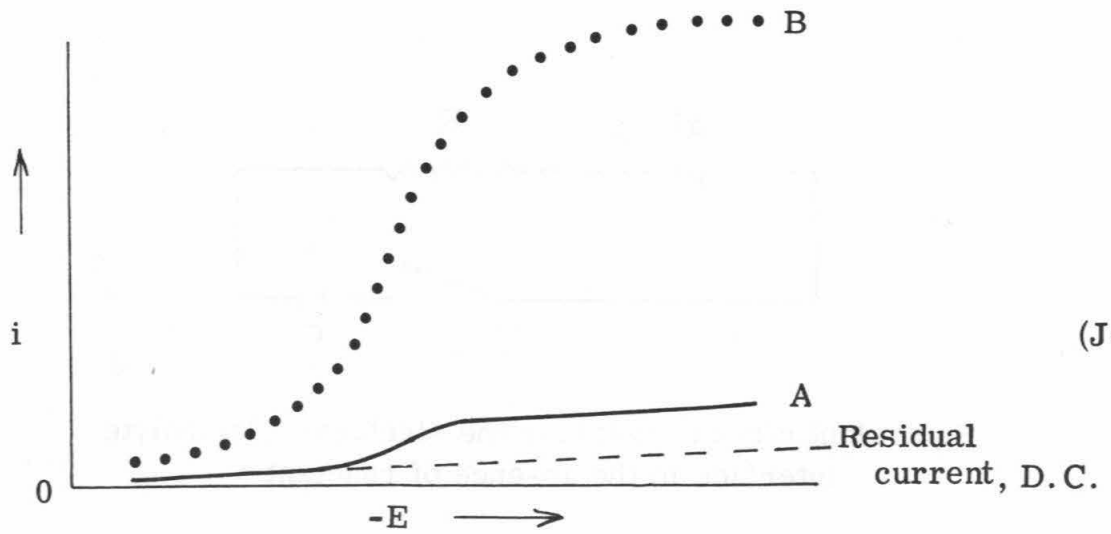
Typical parameters:

$$n = 2;\ D = 10^{-5}\ cm^2\ sec^{-1};\ A = 0.02\ cm^2;\ C^b = 10^{-6}\ M;$$
$$\Delta E = 250\ mV;\ C = 25\ \mu F\ cm^{-1};\ R = 100\ ohms \qquad (J\text{-}7)$$

Time after potential step, msec	$\frac{i_c}{i_f}$ for step to diffusion plateau
0.20	938
0.55	1.4
0.75	.030
1	2×10^{-4}

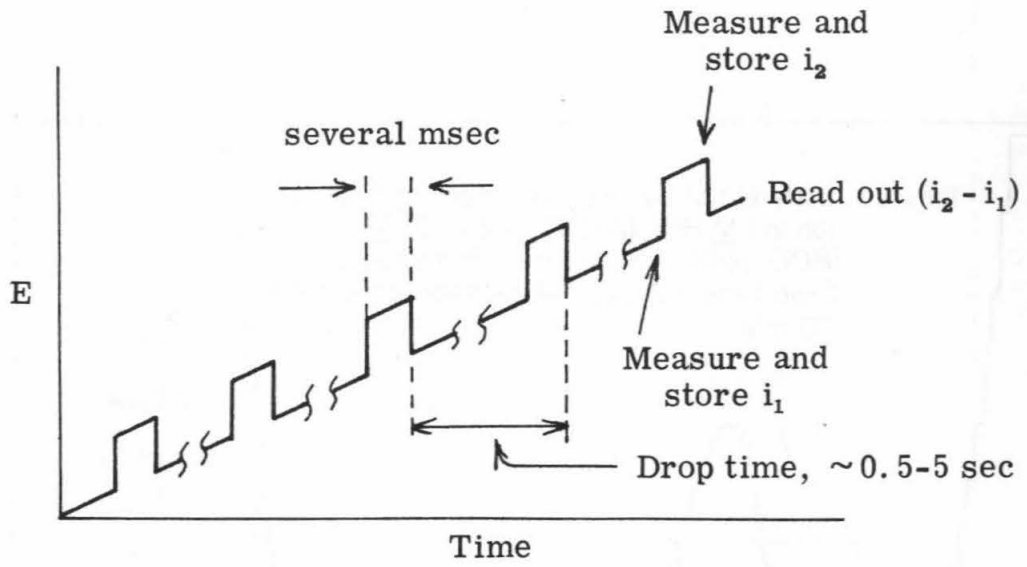
(J-8)

Comparison of D.C. and pulse polarograms with dilute solutions

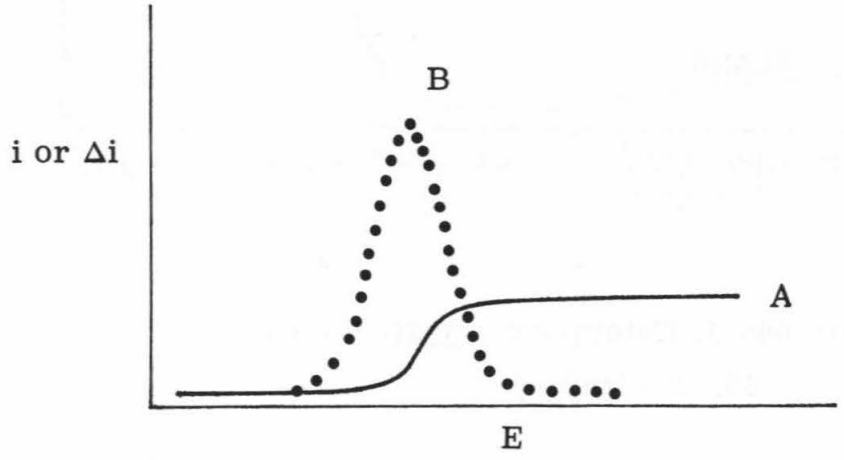


(J-9)

Differential Pulse Polarography



(J-10)



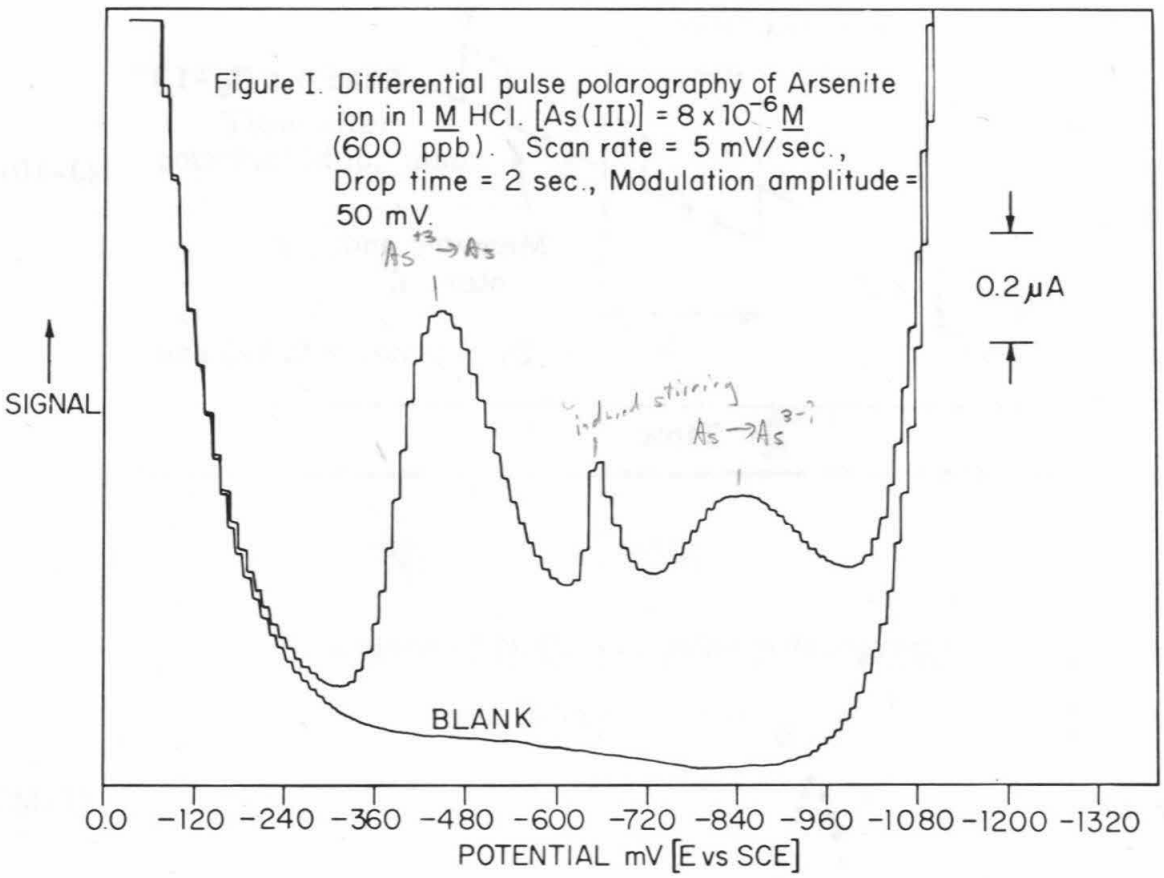
(J-11)

A -- DC Polarogram

B -- Differential pulse polarogram

Examples of Pulse Polarographic Analysis:

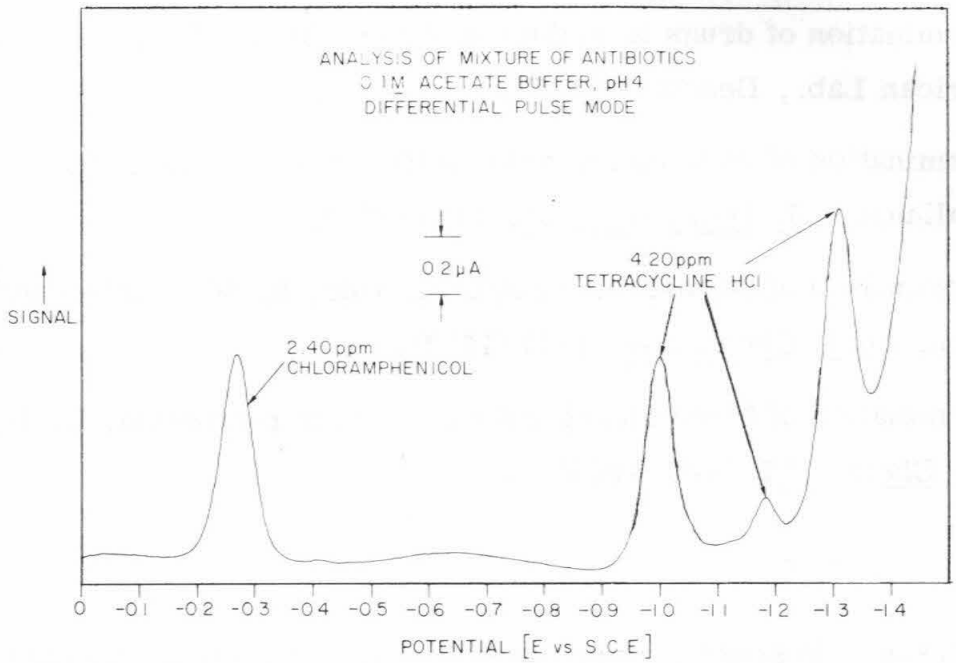
Arsenic:



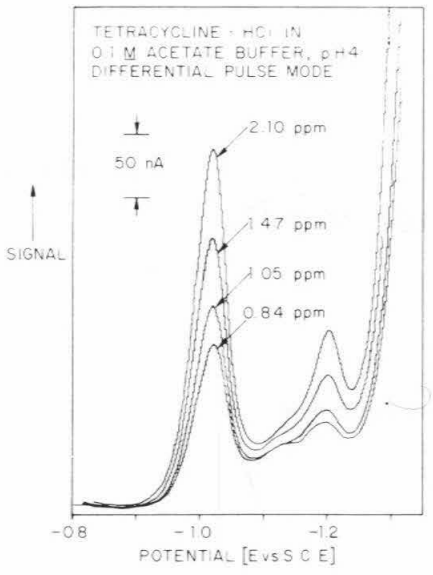
(J-12)

[D. J. Meyers and J. Osteryoung, Anal. Chem., 45, 267 (1973)]

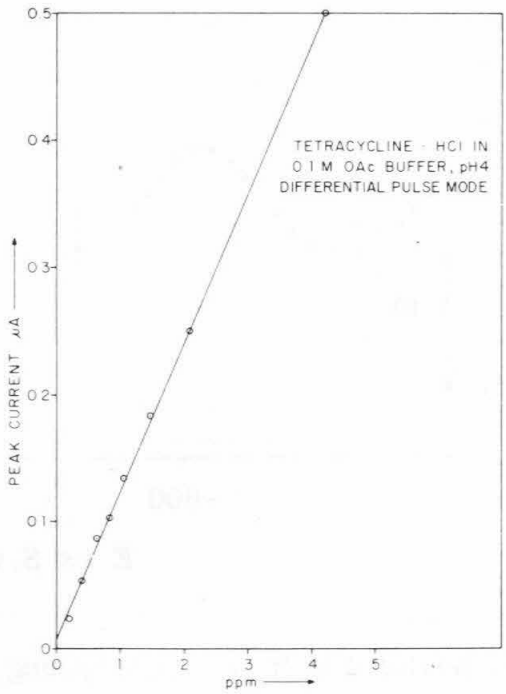
Antibiotics:



(J-13)



(J-14)



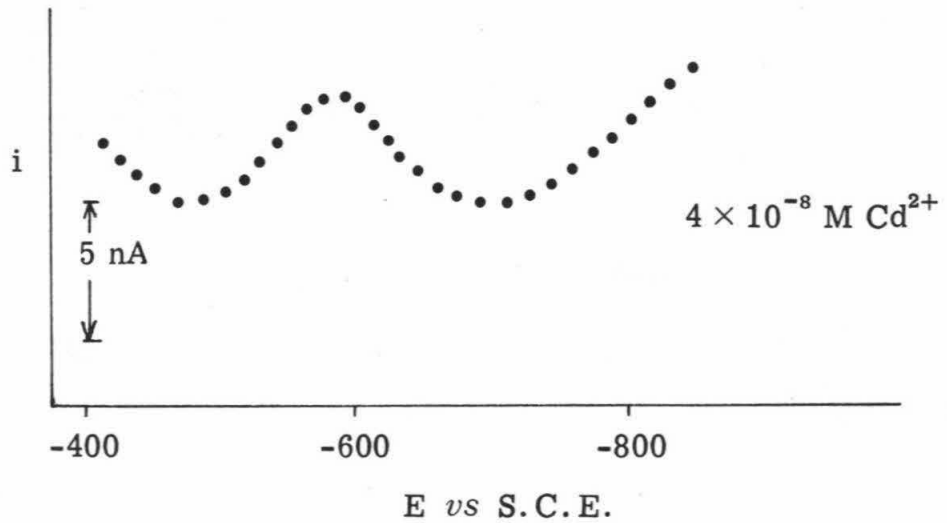
(J-15)

[From Princeton Applied Electronics Application Note 111 (1973)]

Additional Quantitative Analyses by Means of Differential Pulse Polarography: (J-16)

1. Determination of drugs in biological fluids, M. A. Brooks *et al.*, American Lab., December 1973.
2. Determination of cadmium in dried milk, D. G. Cornell and J. Pallansch, J. Dairy Sci., 56, 1479 (1973).
3. Determination of atmospheric sulfur dioxide, R. W. Garber and C. E. Wilson, Anal. Chem., 44, 1357 (1972).
4. Determination of trace nickel and vanadium in petroleum, D. D. Gilbert, Anal. Chem., 37, 1102 (1965).

Great increases in sensitivity are possible with pulse polarography:



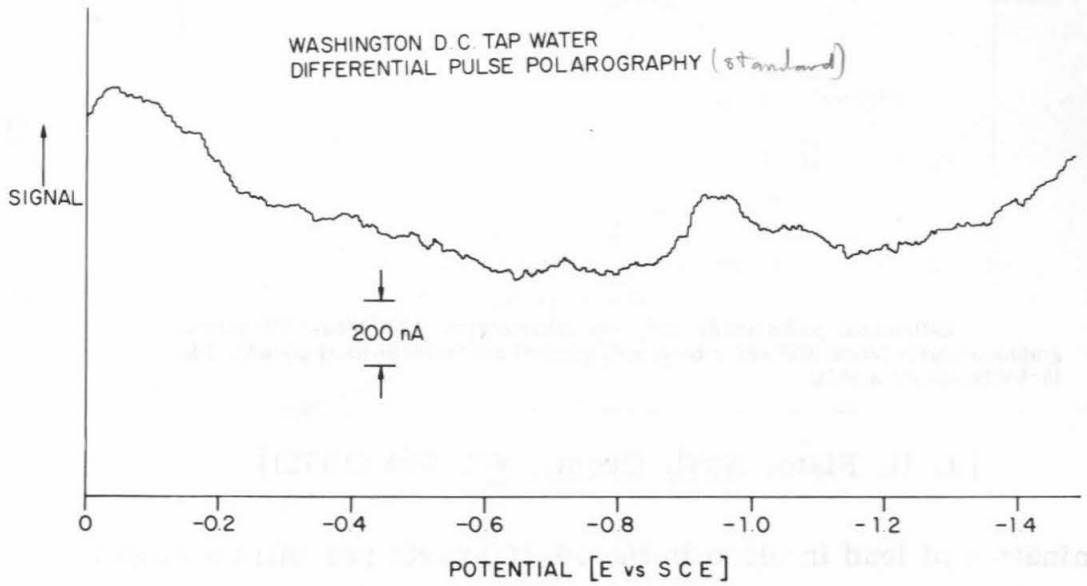
(J-17)

[H. E. Keller and R. A. Osteryoung, Anal. Chem., 43, 342 (1971)]

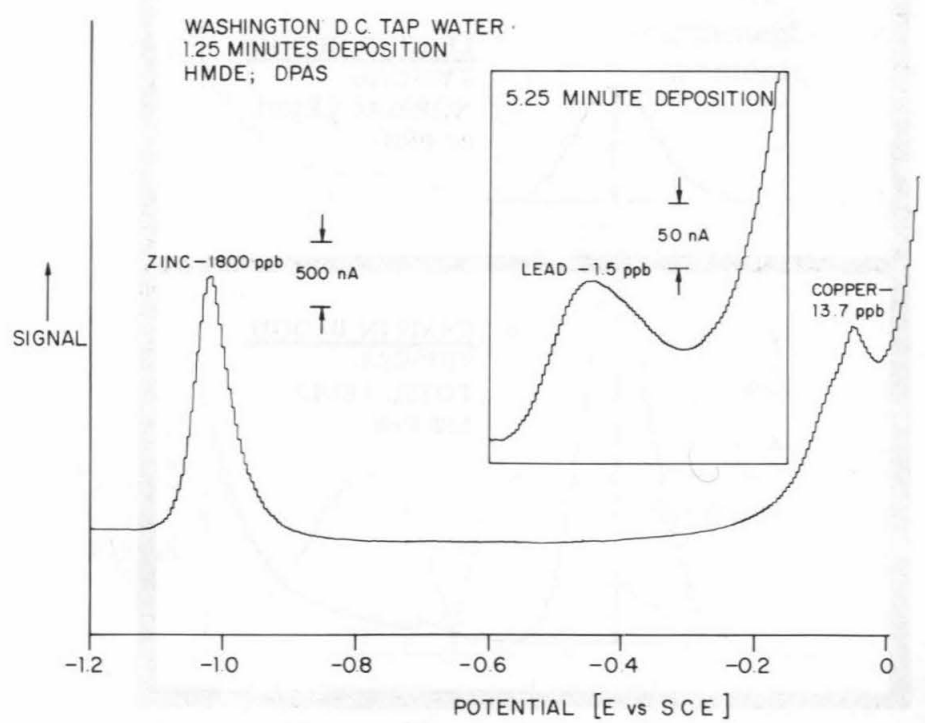
Differential Pulse Polarographic Anodic Stripping Analysis:

1) Concentrate metals by deposition as amalgams on mercury electrode

2) Strip the metals from the amalgam by anodic oxidation

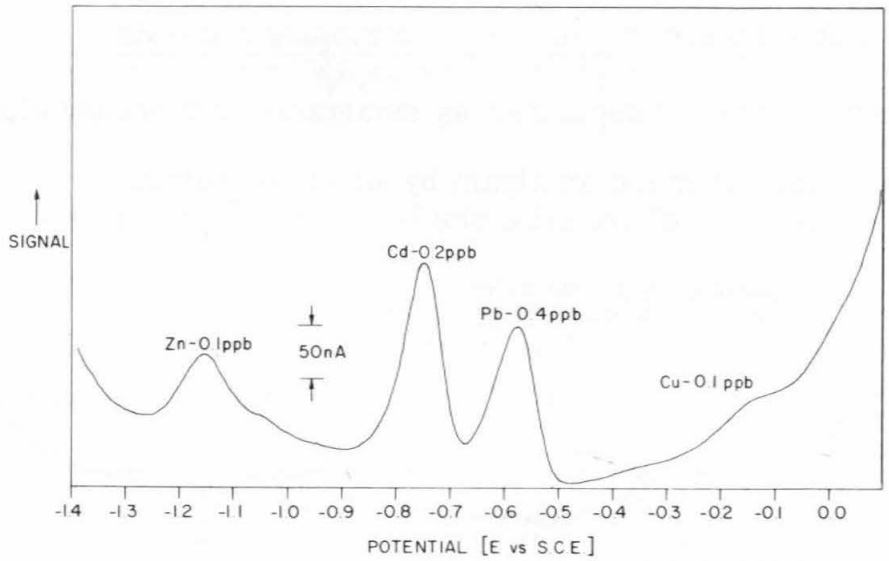


(J-18)



(J-19)

[H. Siegerman and G. O'Dom, American Lab., June (1972)]

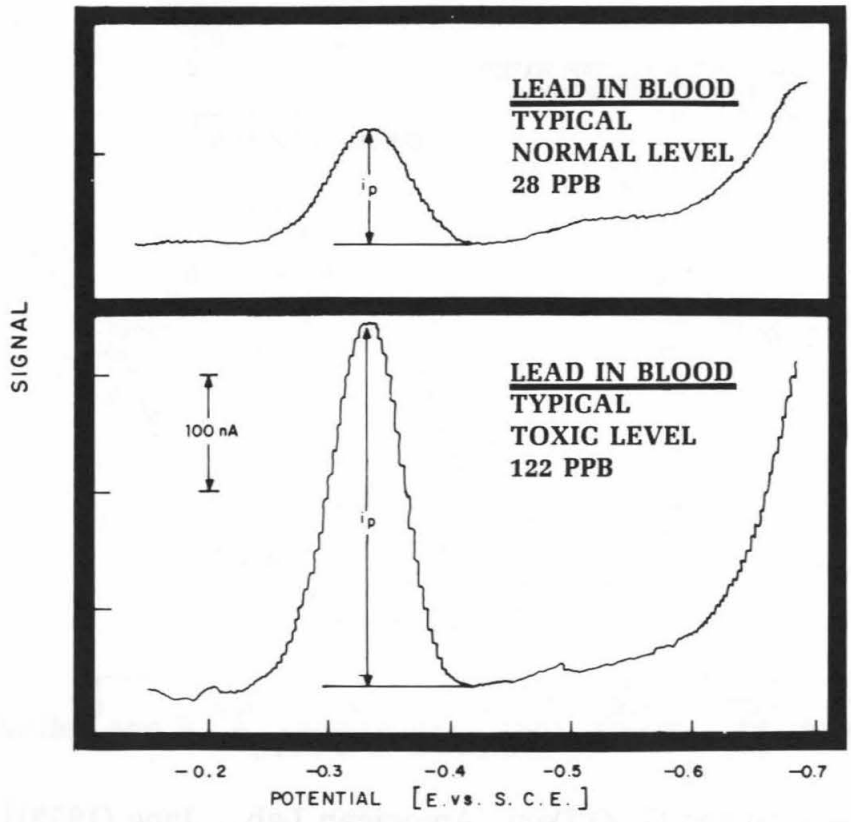


Differential pulse anodic stripping voltammetry. PAR Model 174 polarographic analyzer, Model 9319 wax-impregnated graphite electrode (mercury-plated). $2 \times 10^{-9} M$ Zn, Cd, Pb, and Cu

(J-20)

[J. B. Flato, Anal. Chem., 44, 75A (1972)]

Determination of lead in blood in the 10-100 parts per billion range:

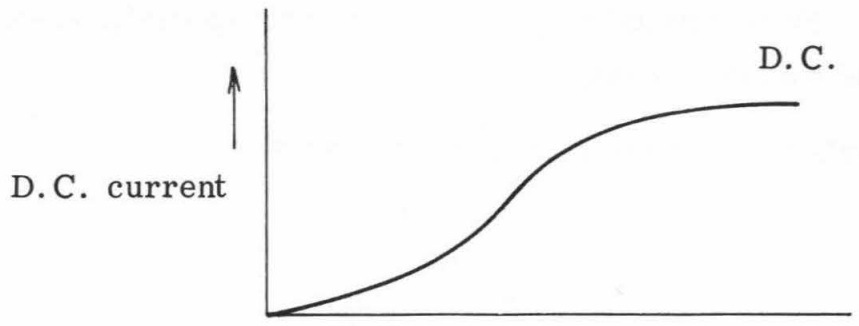


(J-21)

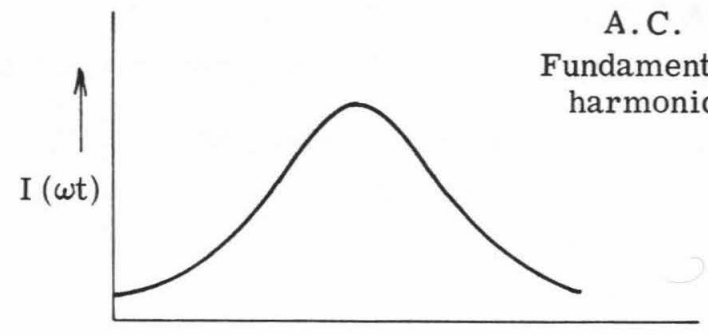
[Princeton Applied Research Application Note 106 (1971)]

Alternating Current Polarography:

Polarograms (current sampling mode)

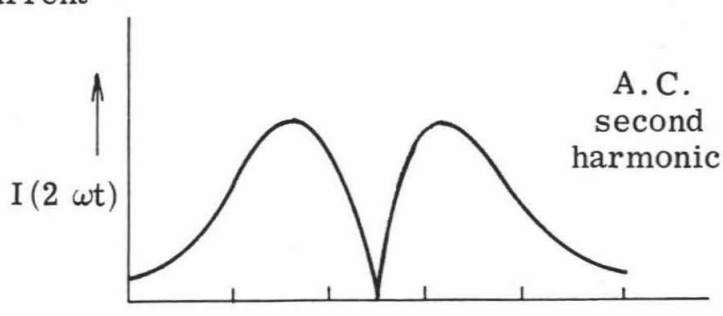


(J-22)



(J-23)

A.C. current



(J-24)

Attractive features of a.c. polarography: (J-25)

- Good discrimination between faradaic and non-faradaic components of current
- Phase sensitive detection readily applied
- Resolution of closely spaced waves is facilitated (especially in the second harmonic mode)
- Oxygen removal is unnecessary in some instances

General References on Pulse Polarography:

1. G. C. Barker and A. W. Gardner, Z. anal. Chem., 173, 79 (1960).

2. E. P. Parry and R. A. Osteryoung, Anal. Chem., 36, 1366 (1964); 37, 1634 (1965); K. B. Oldham and E. P. Parry, Anal. Chem., 42, 229 (1970).

3. D. E. Burge, J. Chem. Educ., 47, A81 (1970).

4. J. Osteryoung and R. A. Osteryoung, Amer. Lab., July, 1972.

5. J. B. Flato, Anal. Chem., 44, 75A (1972).

General References on A.C. Polarography:

1. D. M. Smith, Crit. Rev. Anal. Chem., 2, 247 (1971).

2. D. M. Smith in "Electroanalytical Chemistry," A. J. Bard, Ed., Marcel Dekker, Inc., New York, 1966, Vol. 1, p. 1.

3. B. Breyer and H. N. Bauer, "Alternating Current Polarography and Tensammetry" in "Chemical Analysis," P. J. Elving and I. M. Kolthoff, Eds., Vol. 13, Interscience Publishers, New York, 1963.

4. E. R. Brown and R. F. Large in "Physical Methods of Chemistry, Part IIA: Electrochemical Methods," A. Weissberger and B. W. Rossiter, Eds., Wiley-Interscience, New York, 1971, Ch. VI.

Study Problems:

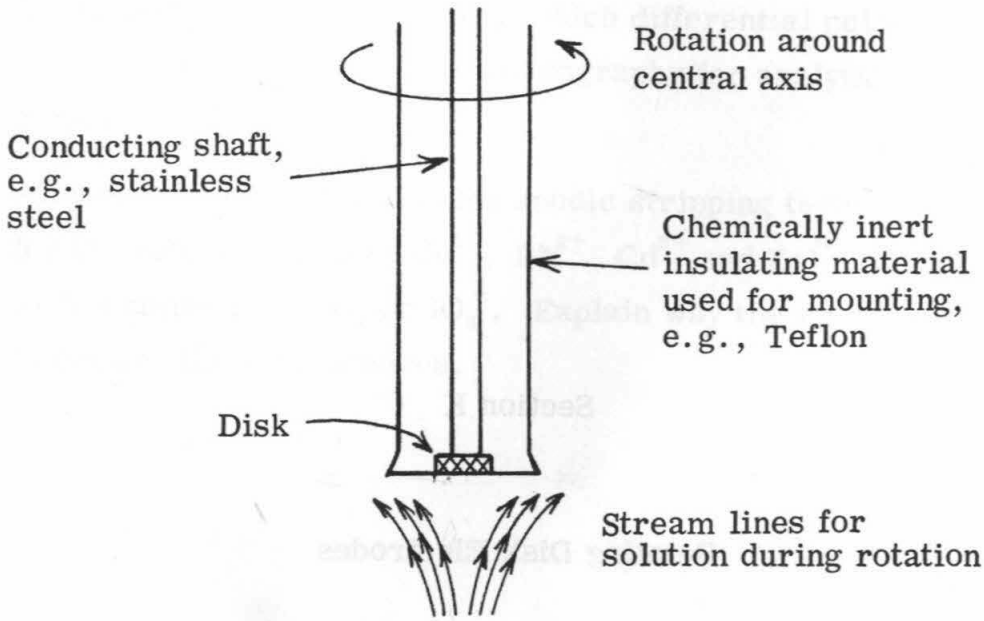
1-J. What causes the non-faradaic charging current in d.c. polarography? In normal pulse polarography?

2-J. Describe two circumstances in which differential pulse polarography is superior to normal pulse polarography for analytical determinations.

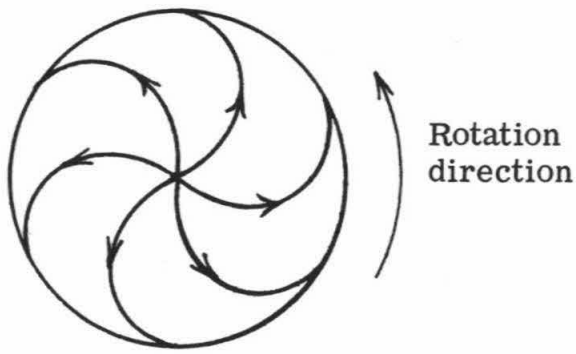
3-J. Although the differential pulse anodic stripping technique works well for the determination of Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}, it cannot be used to determine Hg^{2+}, O_2 or IO_3^-. Explain why the method is not applicable to each of these substances.

Section K

Rotating Disk Electrodes



(K-1)



(K-2)

At disk surface

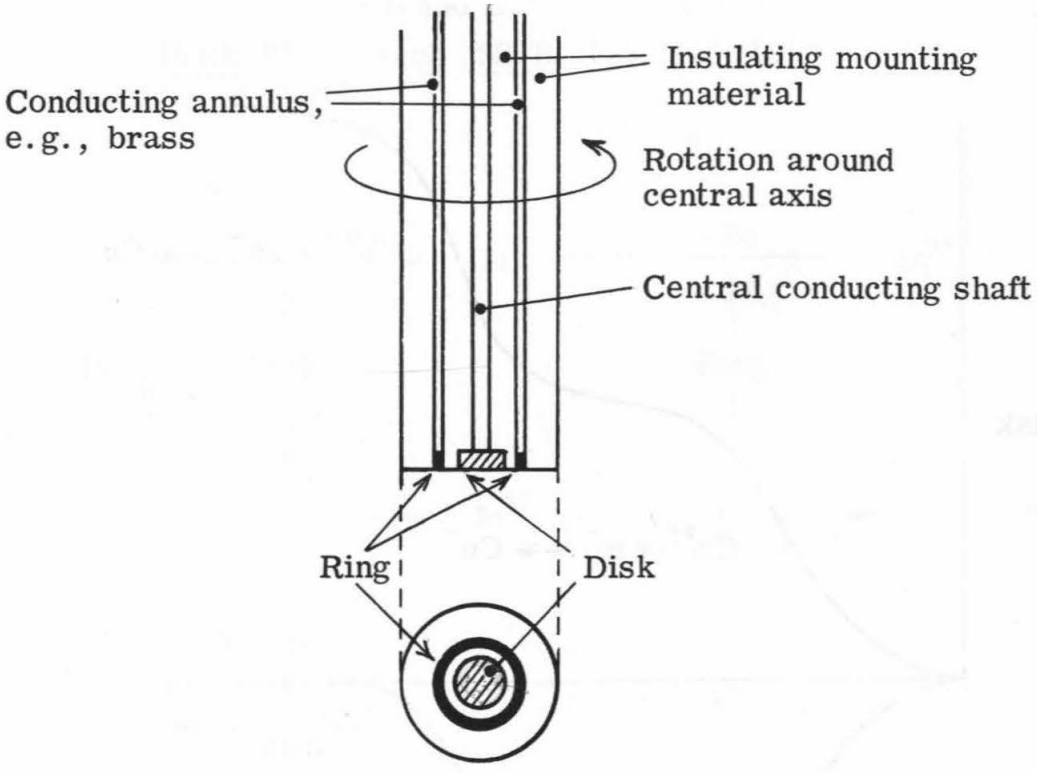
The Levich Equation:

$$i_L = 0.62\, nF\, A\, D^{2/3}\, \nu^{-1/6}\, \omega^{1/2}\, C^b \qquad \text{(K-3)}$$

ν = kinematic viscosity of solution

ω = rotation rate

Ring-Disk Electrode



(K-4)

Disk reaction: $Ox + ne \longrightarrow Red;\quad i_D$ (K-5)

Ring reaction: $Red \longrightarrow Ox + ne^-;\quad i_R$ (K-6)

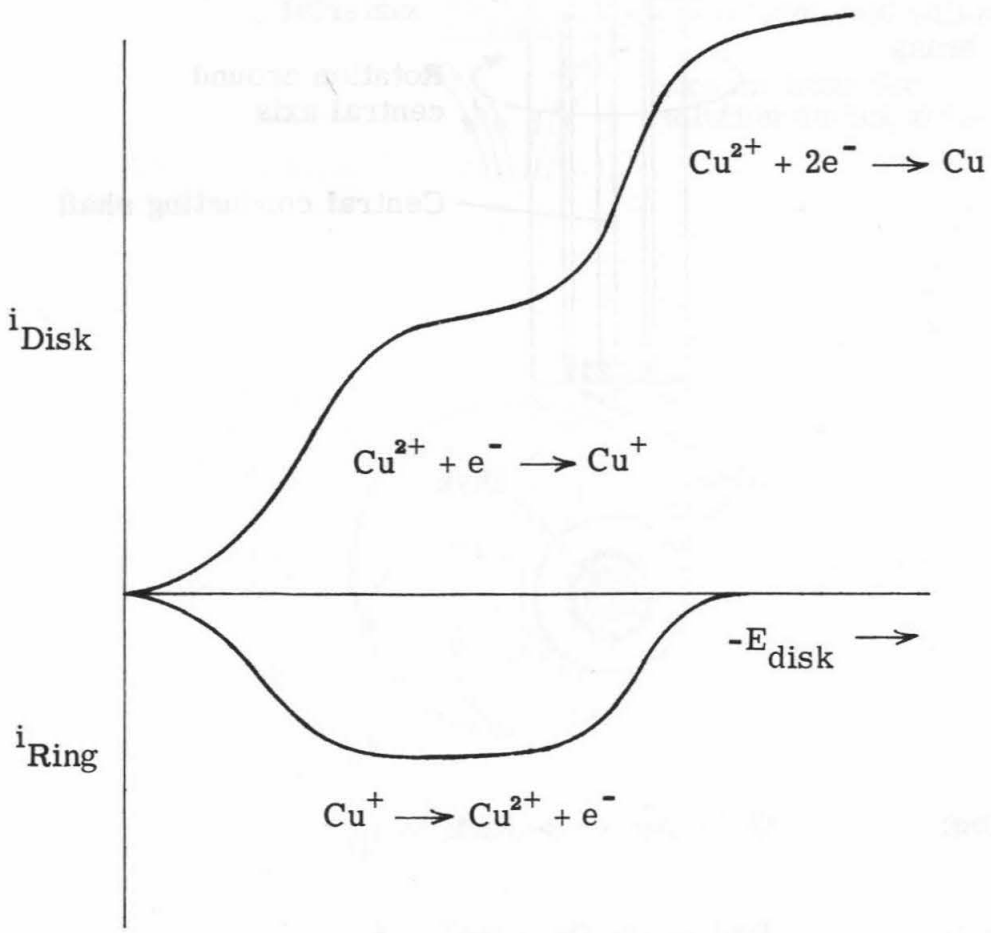
Example: Cu(II) in chloride solution

At disk:

first wave: $Cu^{2+} + e^- \xrightarrow{KCl} Cu^+(CuCl_2^-)$

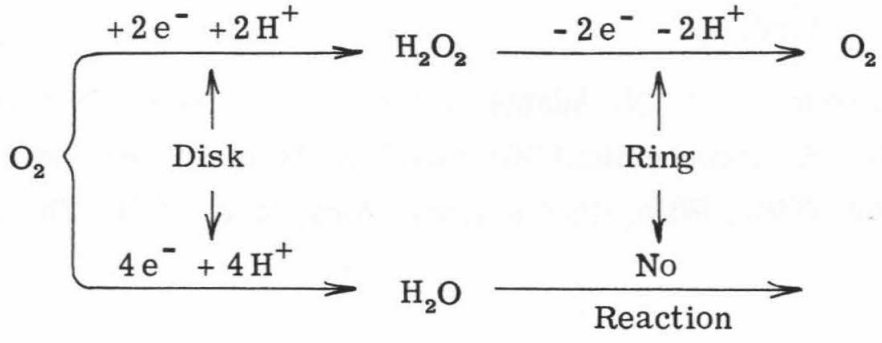
second wave: $Cu^{2+} + 2e^- \longrightarrow Cu$ (K-7)

At ring: $Cu^+ \longrightarrow Cu^{2+} + e^-$

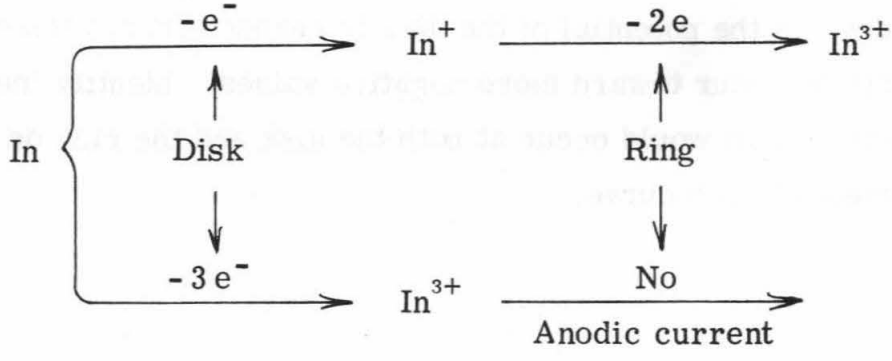


(K-8)

Other examples:



[A. N. Frumkin and L. N. Nekrasov,
Dokl. Akad. Nauk SSSR, 126, 115 (1959)]



[B. Miller and R. E. Visco,
J. Electrochem. Soc., 115, 251 (1968)]

General References:

1. "Ring-Disk Electrodes," W. J. Albery and M. L. Hitchman, Clarendon Press, Oxford, 1971.

2. S. Piekarski and R. N. Adams in "Physical Methods of Chemistry, Part IIA: Electrochemical Methods," A. Weissberger and B. W. Rossiter, Eds., Wiley-Interscience, New York, 1971, Ch. VII.

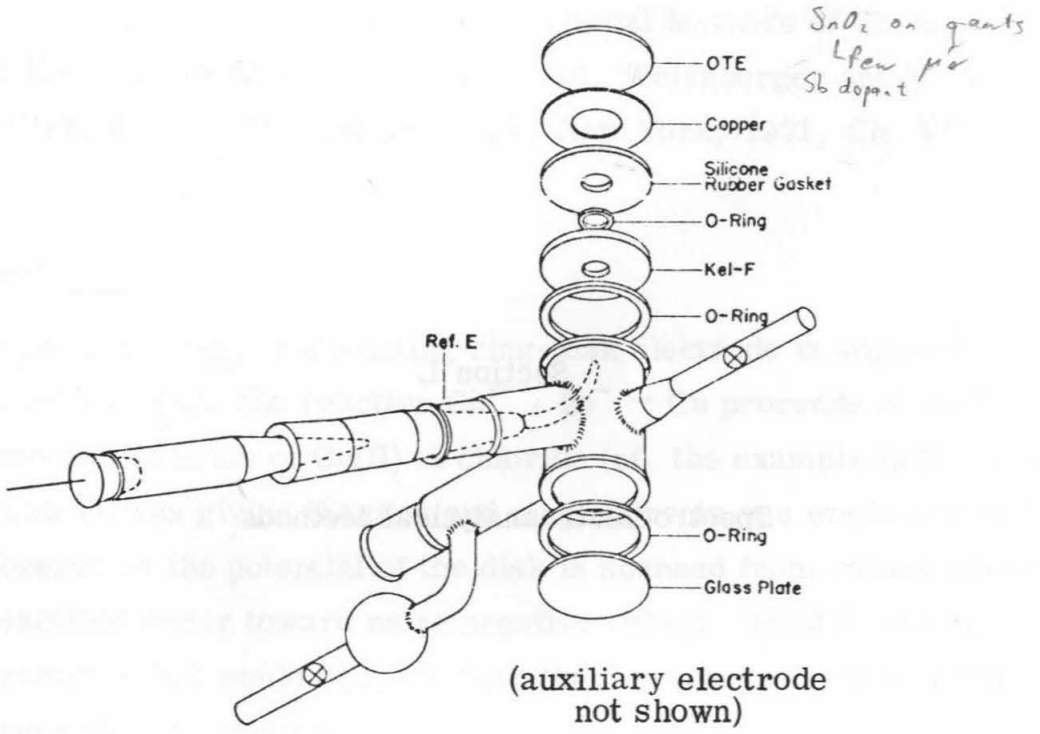
Study Problem:

1-K. Suppose the ring of a rotating ring-disk electrode is adjusted to a potential where the reaction $Cu^{2+} + 2e^- \rightarrow Cu$ proceeds at its limiting rate in a solution of Cu(II) in chloride (cf. the example in K-7 and K-8). Draw curves giving the disk and ring currents you would expect to observe as the potential of the disk is scanned from values where no reactions occur toward more negative values. Identify the electrode reactions that would occur at both the disk and the ring on each segment of each curve.

Section L

Spectroelectroanalytical Methods

A Cell Employing an Optically Transparent Electrode (OTE) made of SnO_2:



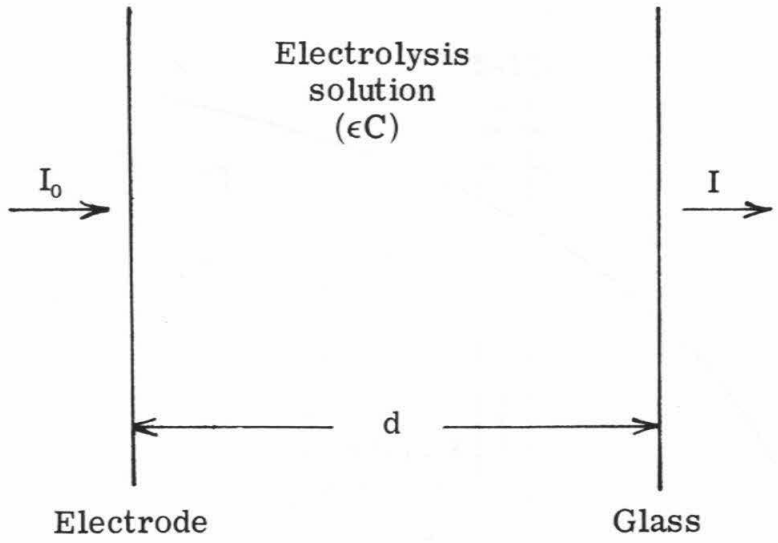
(L-1)

Sandwich cell for transmission experiments.

[T. Kuwana and N. Winograd in, "Electroanalytical Chemistry," A. J. Bard, Ed., M. Dekker, Inc., New York, 1974, Vol. 7]

Optical Responses at Transparent Electrodes:

Transmission mode:



(L-2)

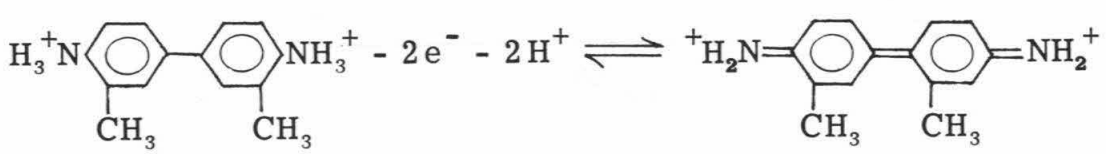
$$A = \log \frac{I_0}{I} = \epsilon d C(t) \qquad \text{(L-3)}$$

For chronoamperometric conditions:

$$A = \epsilon C^b \times 2\left(\frac{Dt}{\pi}\right)^{1/2} \qquad \text{(L-4)}$$

$$\text{Diffusion layer thickness} = 2\left(\frac{Dt}{\pi}\right)^{1/2} \Rightarrow d \qquad \text{(L-5)}$$

Example: Oxidation of *o*-tolidine in a transmission cell

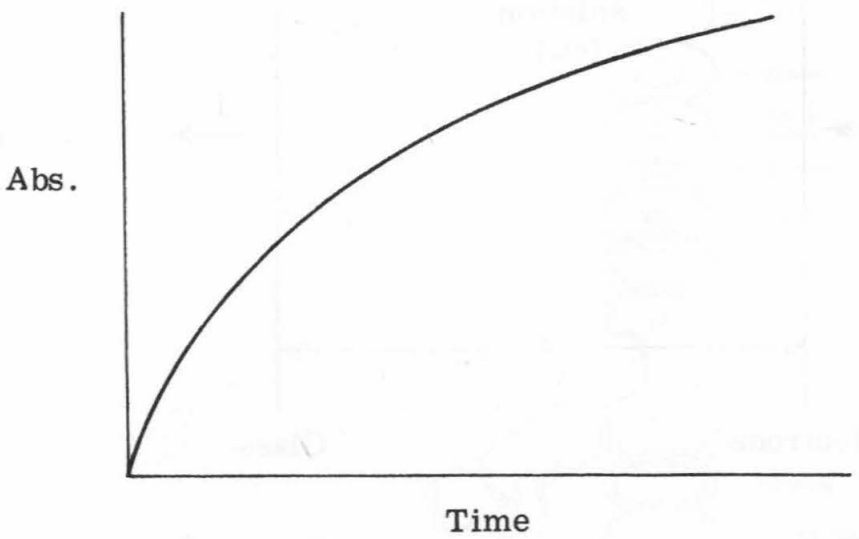


(L-6)

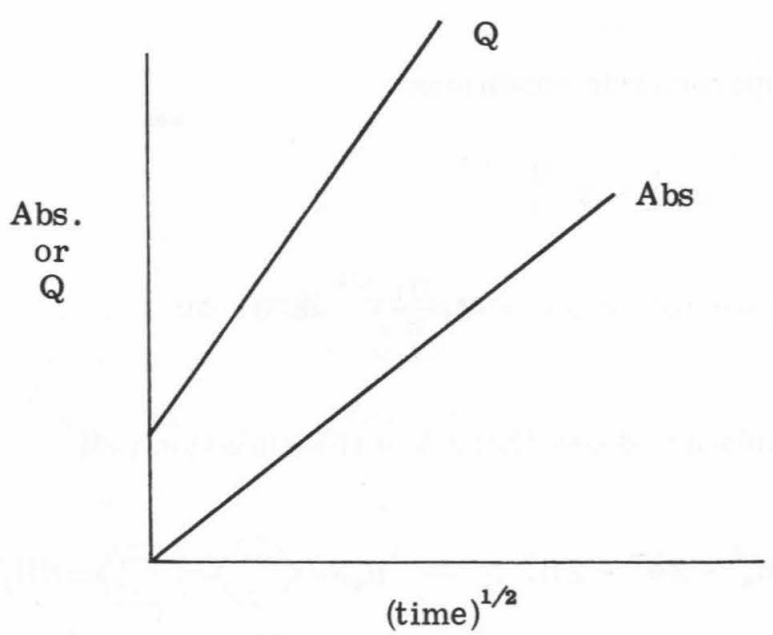
λ_{max} = 438 nm

Charge-time and Absorbance-time Response

During Oxidation of o-tolidine



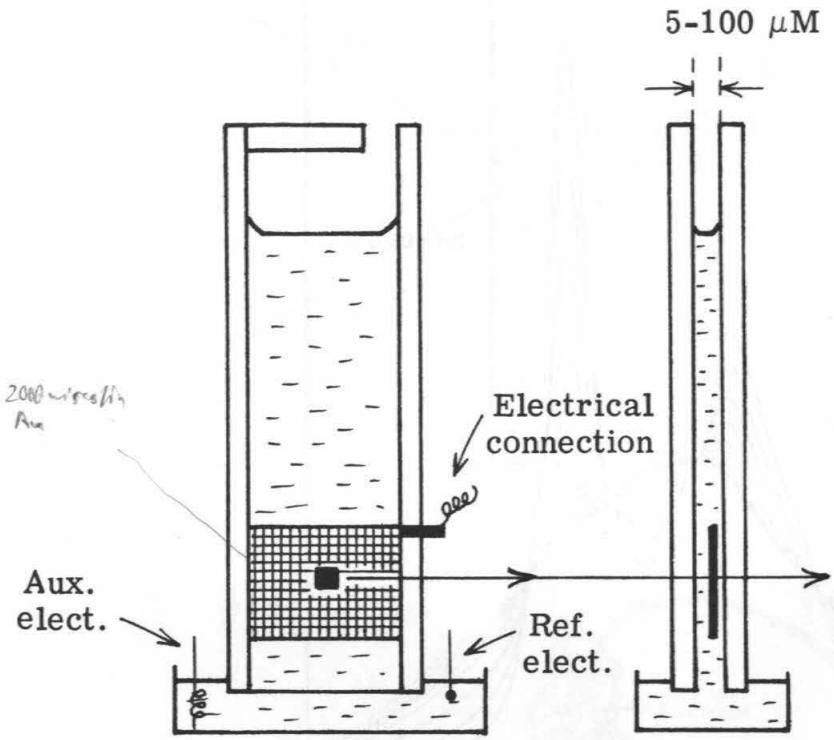
(L-7)



(L-8)

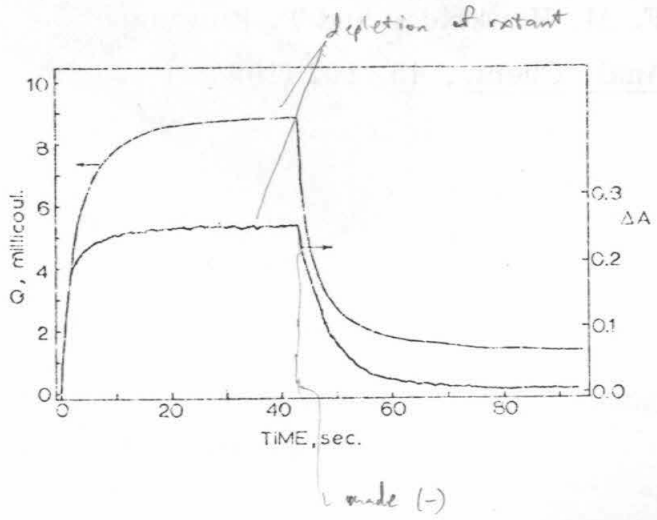
Thin-Layer Cells:

Minigrid Electrode [R. W. Murray, W. R. Heineman and G. W. O'Dom, Anal. Chem., 39, 1666 (1967)]:



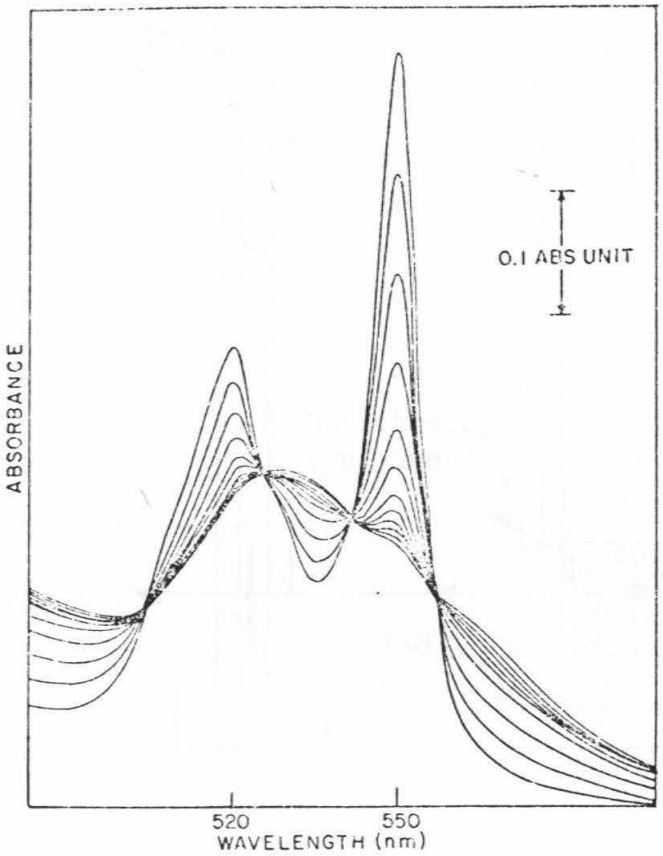
(L-9)

Charge-Time and Absorbance-Time Response During Oxidation of o-tolidine



(L-10)

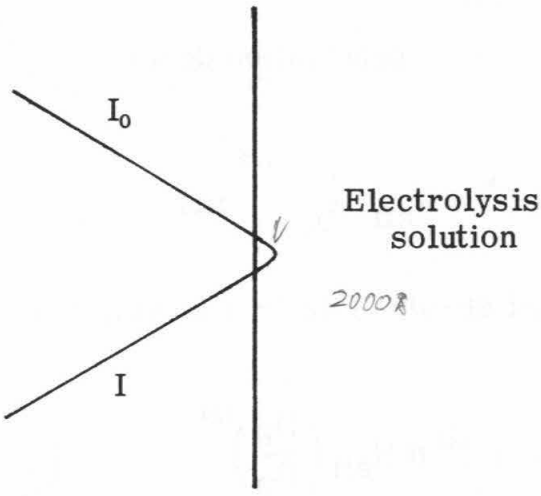
Spectra of Cytochome *c* Solutions



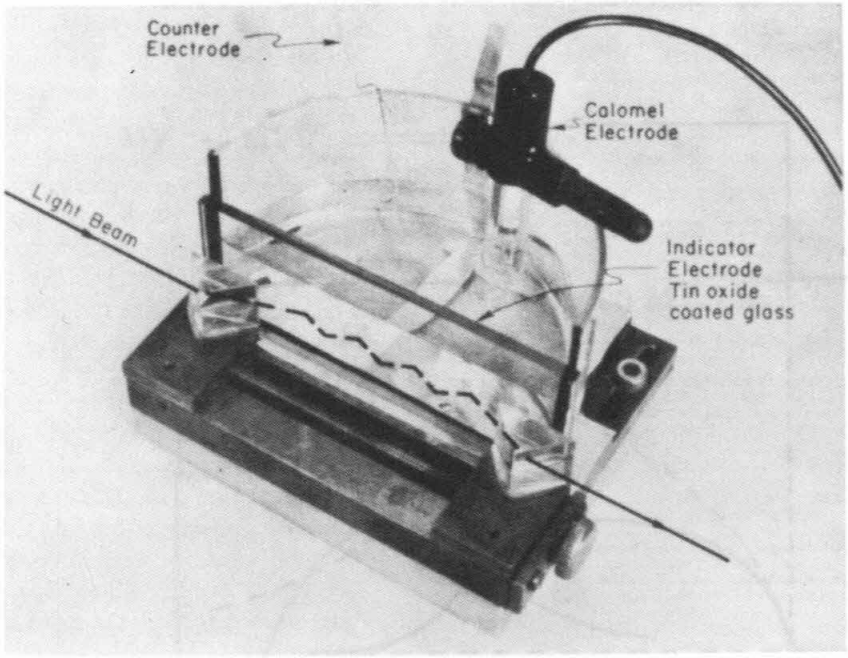
(L-11)

[F. M. Hawkridge and T. Kuwana, Anal. Chem., 45, 102 (1973).]

Internal Reflection Spectroelectrochemistry



(L-12)



(L-13)

[W. N. Hansen, T. Kuwana and R. A. Osteryoung, Anal. Chem., 38, 1810 (1966).]

$$A = \log \frac{I_0}{I} = N_{eff} \times \epsilon d C \qquad \text{(L-14)}$$

N_{eff} = "sensitivity factor" — char. of electrode opt. char. of exp

d = penetration depth

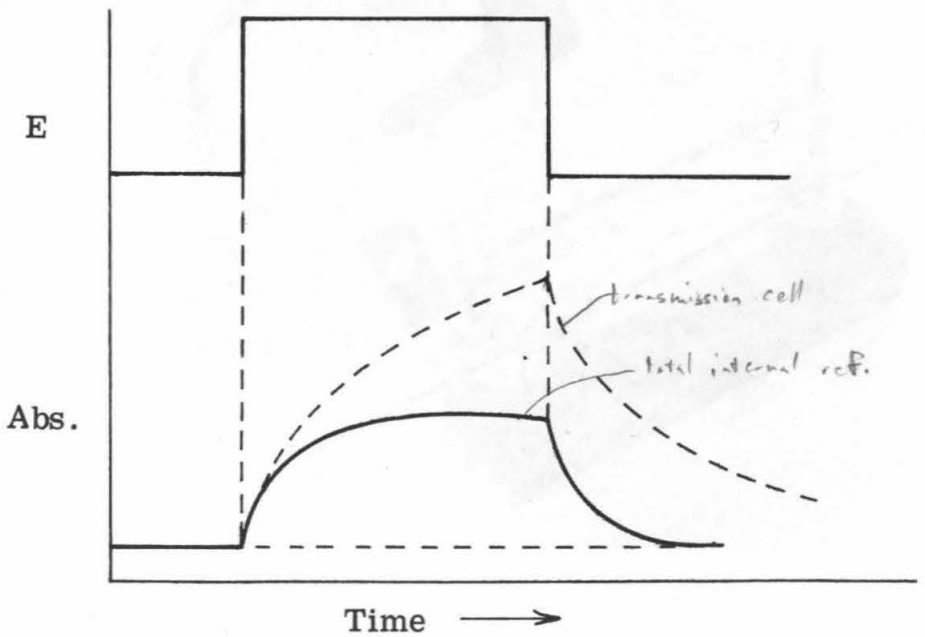
$$A = \epsilon C^b d N_{eff} \left(\frac{D_R}{D_P}\right)^{1/2} f(t) \qquad \text{(L-15)}$$

(reactant / product)

At steady state (~ 1 msec), $f(t) \rightarrow 1$

$$A = \epsilon C^b d N_{eff} \left(\frac{D_R}{D_P}\right)^{1/2} \qquad \text{(L-16)}$$

Chronoamperometry with o-tolidine



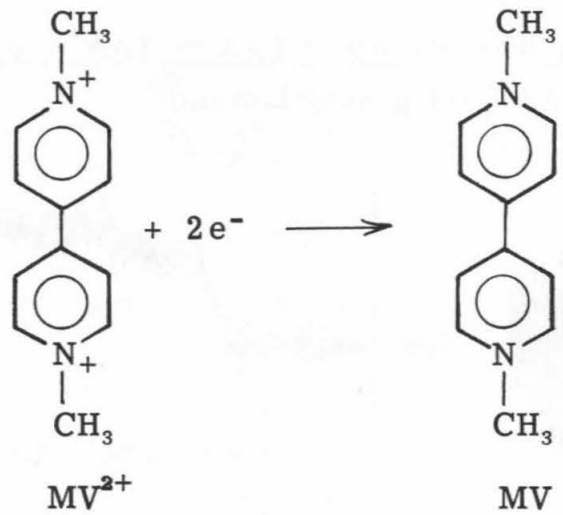
(L-17)

[Adapted from W. N. Hansen, T. Kuwana and R. A. Osteryoung, Anal. Chem., 38, 1810 (1966).]

Application in Solution Kinetics

Reproportionation of Methyl Viologen Cationic Radicals:

[After N. Winograd and T. Kuwana,
J. Amer. Chem. Soc., 92, 224 (1970).]

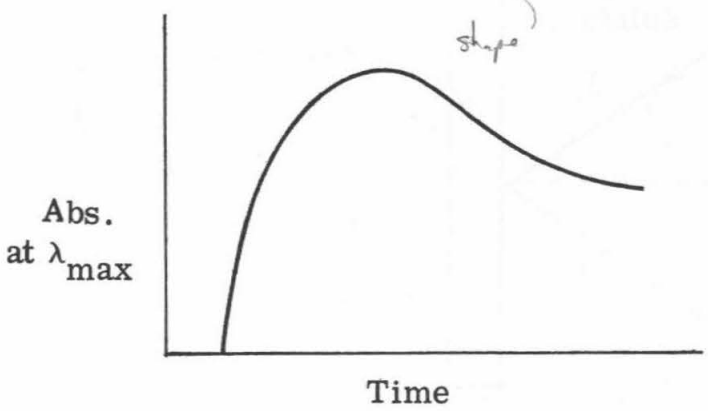


(L-18)

$$MV + MV^{2+} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2MV^{+\cdot} \qquad \text{(L-19)}$$

λ_{max} = 605 nm

ϵ = 20,000 M^{-1} cm^{-1}



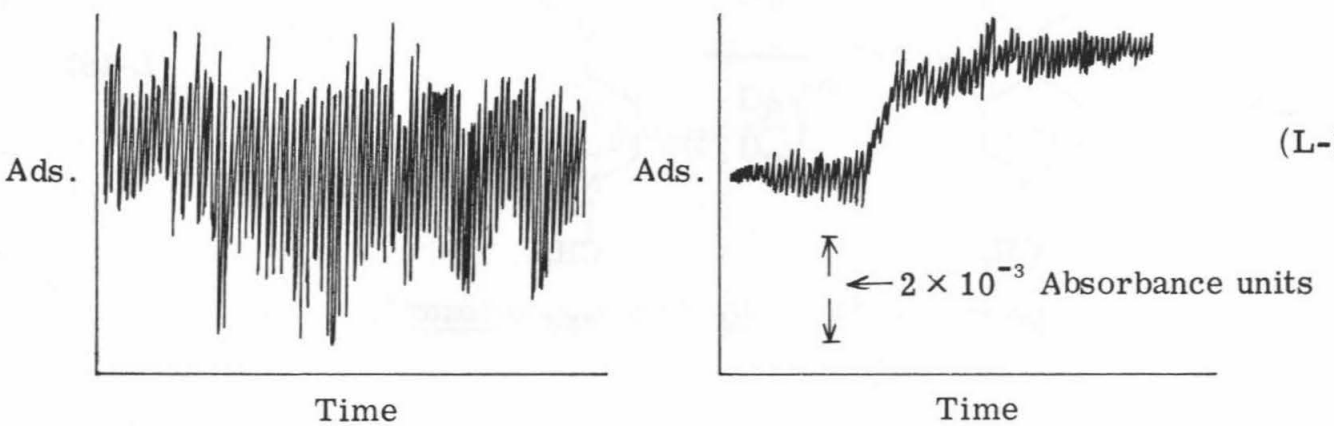
(L-20)

Special virtues of internal reflection spectroelectrochemistry:

- Optical response limited to solution within ~ 1000 Å of electrode surface
- Fast "filling" and "dumping" of optically responsive solution layer facilitates signal averaging

(L-21)

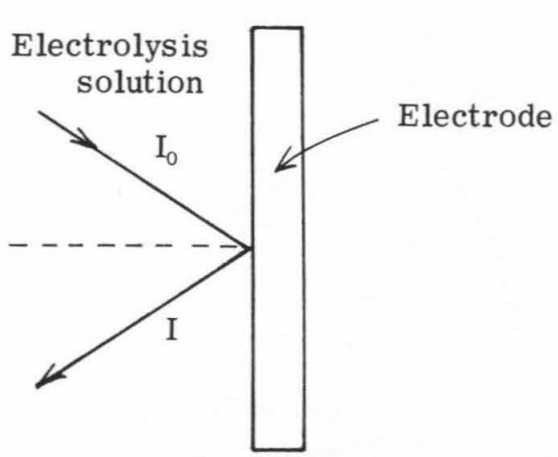
Signal Averaging During 4000 Cycles of TAA → $TAA^+ + e$ → TAA - e
(TAA = tri-p-anisylamine)



(L-22)

[After N. Winograd and T. Kuwana, Anal. Chem., 43, 252 (1972)]

Specular Reflectance

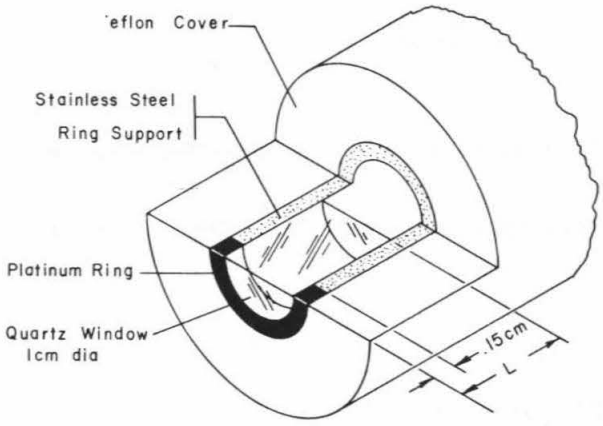


(L-23)

Changes in surface reflectance are measured.

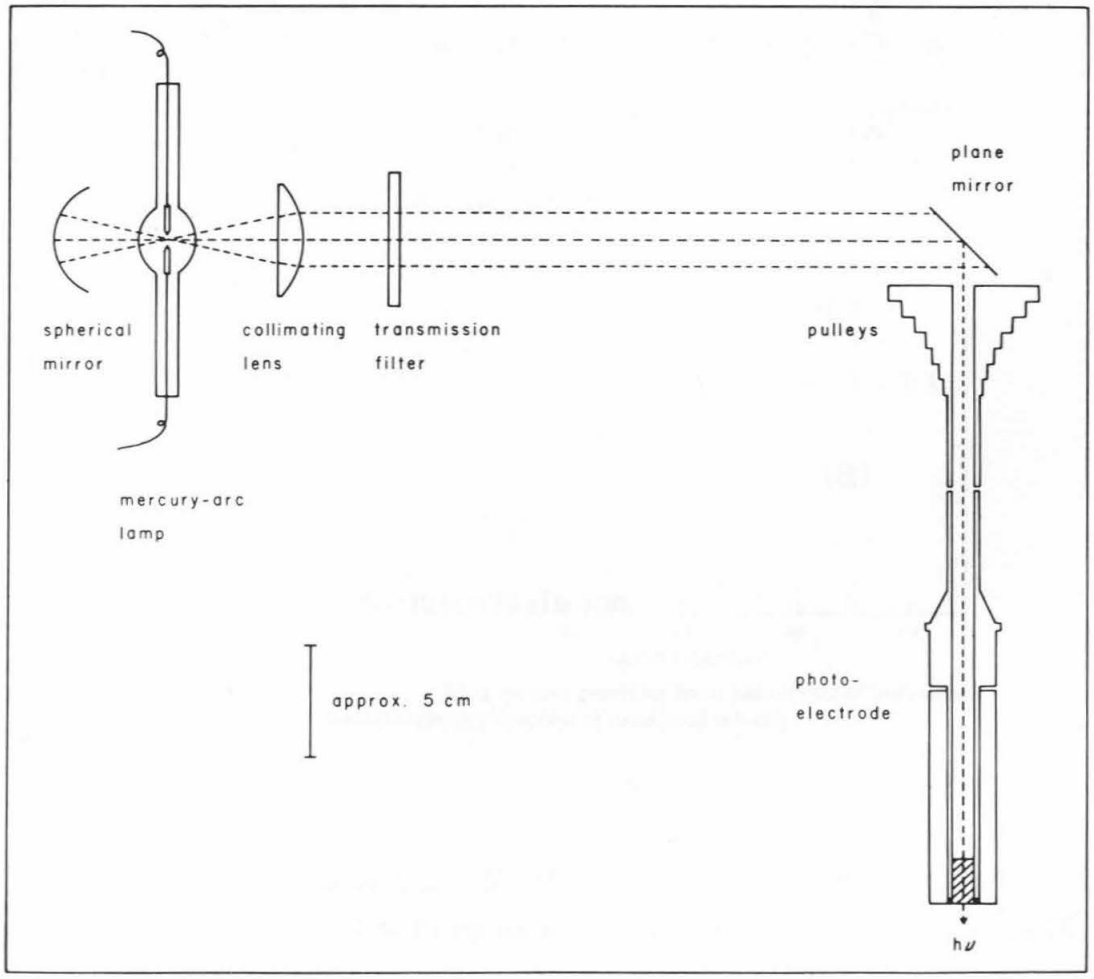
Rotating Ring-Disk Photoelectrode:

[D. C. Johnson and E. W. Resnick, Anal. Chem., 44, 637 (1972)]



Schematic diagram of the photoelectrode

(L-24)



Schematic diagram of the optical system associated with use of the photoelectrode

(L-25)

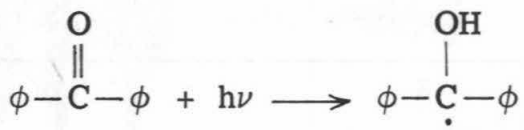
At quartz disk: $A + h\nu \longrightarrow B$ (L-26)

Chemical reaction: $B \xrightarrow{k} C$ (L-27)

B electroactive: I_p increases with ω

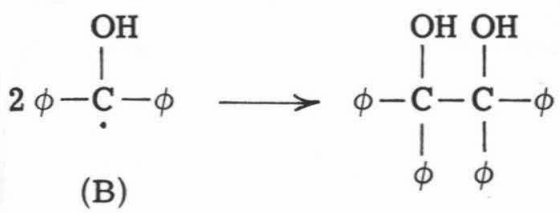
C electroactive: I_p decreases with ω

Photo-pinacolization of benzophenone:



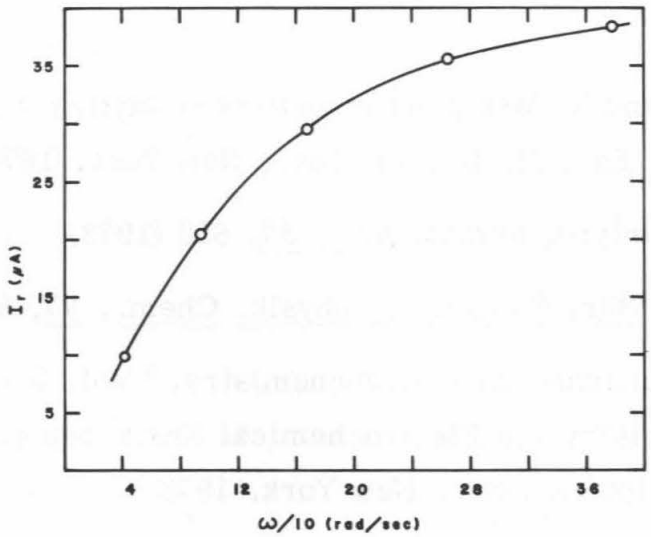
(A) (B) (L-28)

electroactive



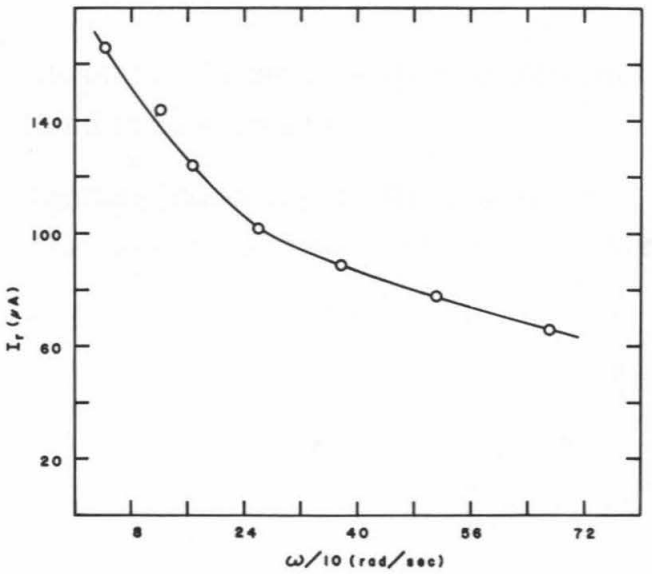
(B) (C) (L-29)

not electroactive



(L-30)

Ring current resulting from photolysis of benzophenone as a function of rotational velocity



(L-31)

Ring current resulting from photolysis of potassium ferrioxalate as a function of rotational velocity

[D. C. Johnson and E. W. Resnick, Anal. Chem., 44, 637 (1972); See also J. R. Labbers *et al.*, Anal. Chem., 46, 865 (1974)]

General References on Spectroelectroanalytical Methods:

1. T. Kuwana and N. Winograd in "Electroanalytical Chemistry," A. J. Bard, Ed., M. Dekker, Inc., New York, 1974, Vol. 7.

2. J. D. E. McIntyre, Surface Sci., 37, 658 (1973).

3. T. Kuwana, Ber. Bunsenges. physik. Chem., 77, 858 (1973).

4. "Optical Techniques in Electrochemistry," Vol. 9 of "Advances in Electrochemistry and Electrochemical Engineering," R. H. Muller, Ed., Wiley-Interscience, New York, 1973.

Section M

Appendix

1. Glossary of Electroanalytical Nomenclature Used in this Course
2. Leading Monographs, Review Series and Journals in Electroanalytical Chemistry
3. Solutions to Study Problems

1. Glossary of Electroanalytical Nomenclature

Alternating Current Polarography -- A form of polarography in which a small sinusoidal voltage is superimposed on the slowly varying d.c. potential of the electrode and the resulting alternating current is observed.

Amperometric End Point -- A method for detecting end points in coulometric (or other) titrations based on changes in the current flowing through a pair of indicating electrodes between which a small constant voltage is maintained. The name is also applied to end points determined from currents flowing through a single indicating electrode whose potential is maintained at an appropriate value with respect to a reference electrode.

Anodic Stripping -- A type of voltammetry, usually conducted with hanging mercury drop or mercury film electrodes in which metal amalgams are formed by pre-electrolysis with a stirred solution. The concentrations of the metals present in the solutions are determined from the anodic currents which result when the metal amalgams are "stripped" from the electrode by anodic oxidation.

Auxiliary Electrode -- The electrode used to complete the current measuring circuit in three-electrode electrolysis cells.

Chronoamperometry -- Observation of the current flowing as a function of time following the sudden application of a potential to the working electrode which causes a reaction to proceed. The solution is not stirred.

Chronocoulometry -- Observation of the charge passed as a function of time following the sudden application of a potential to the working electrode which causes a reaction to proceed. The solution is not stirred.

Chronopotentiometry -- Observation of the potential of the working electrode as a function of time while a constant current is passed through it.

Controlled Potential Electrolysis -- Electrolysis experiments conducted in stirred solutions with the working electrode maintained at a constant potential *vs* the reference electrode. If the electrical charge passed during the electrolysis is measured, the method is termed controlled potential coulometry.

Coulometric Titrations -- Analytical titrations in which the titrant is generated electrochemically from a reagent precursor, usually with a constant generating current.

Coulometry -- Electrochemical measurements based on Faraday's Law relating the quantity of chemical change with the amount of electrical charge passed.

Cyclic Voltammetry -- Voltammetry conducted with a working electrode whose potential is caused to cycle between two selected values.

Diffusion Layer -- A thin layer of solution at the surface of an electrode within which mass transfer occurs by diffusion.

Faradaic Currents -- Currents arising from the occurrence of electrode reactions (which Faraday's Law governs).

Flux -- The rate of movement of material across a specified plane in moles cm^{-2} sec^{-1}.

Indicator Electrode -- The electrode of primary interest in an electrolysis cell. The electrode reaction being investigated occurs at this electrode. The IUPAC recommends that "indicator electrode" be used in situations where the electrolysis results in no significant changes in the bulk concentration of the reactant. When the contrary is true "working electrode" is recommended.

Limiting Current -- That value of the current passing through an electrode which remains constant over a range of electrode potentials.

Nernstian -- Adjective used to indicate electrode reactions for which the concentrations of reactants and products in the layer of solution next to the electrode surface adhere to the Nernst equation while current is flowing.

Non-Faradaic Currents -- Electrical currents arising from processes occurring at an electrode which do not involve electrode reactions and produce no chemical changes. Currents required to charge and discharge the capacitance present at all electrode-electrolyte interfaces.

Polarography -- Voltammetry performed with the dropping mercury electrode (d.m.e.).

Pulse Polarography -- A form of polarography in which the current resulting from a step change in the electrode potential is sampled once (normal) or twice (differential) over a selected short fraction of the life of the d.m.e. rather than continuously.

Transition Time -- The parameter measured in chronopotentiometric experiments. It is the time required to reduce the concentration of the reactant at the surface of the electrode to zero by passage of a constant current.

Voltammetry -- The general name applied to measurements of the effect of the potential of an electrode in an electrolysis cell on the current that flows through it.

Working Electrode -- The electrode where the reaction of interest proceeds in an electrolysis which results in substantial changes in the bulk concentration of the reactant. If only negligible changes in the bulk composition are produced IUPAC recommends that "indicator electrode" be used.

2. Leading Monographs, Review Series and Journals in Electroanalytical Chemistry

Monographs of Relevance to Electroanalytical Chemistry

"Polarography," I. M. Kolthoff and J. J. Lingane, Interscience Publishers, New York, 1952.

"New Instrumental Methods in Electrochemistry," P. Delahay, Interscience Publishers, New York, 1954.

"Electroanalytical Chemistry," J. J. Lingane, Interscience Publishers, New York, 1958.

"Polarographic Techniques," L. Meites, Interscience Publishers, New York, 1965.

"Principles of Polarography," J. Heyrovsky and J. Kuta, Academic Press, New York, 1966.

"Electrochemistry at Solid Electrodes," R. N. Adams, Marcel Dekker, Inc., New York, 1969.

"Electrochemical Reactions in Nonaqueous Systems," C. K. Mann and K. K. Barnes, Marcel Dekker, Inc., New York, 1970.

"Modern Electrochemistry," J. O'M. Bockris and A. K. Reddy, Plenum Press, New York, 1970.

"A Guide to the Study of Electrode Kinetics," H. R. Thirsk and J. A. Harrison, Academic Press, New York, 1972.

"Introduction to Organic Electrochemistry," M. R. Rifi and F. H. Covitz, Marcel Dekker, Inc., New York, 1974.

"Experimental Electrochemistry for Chemists," D. T. Sawyer and J. L. Roberts, Jr., John Wiley & Sons, New York, 1974.

Continuing Review Series Concentrating on Electroanalytical Topics

"Electroanalytical Chemistry: A Series of Advances," A. J. Bard, Ed., Marcel Dekker, Inc., New York.

"Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and C. Tobias, Eds., Interscience Publishers, New York.

"Modern Aspects of Electrochemistry," J. O'M. Bockris and B. Conway, Eds., Plenum Press, New York.

Annual Reviews of Analytical Chemistry--Fundamental Topics, published biannually in the journal Analytical Chemistry.

Annual Reports to the Chemical Society--Electrochemistry, The Chemical Society, London.

Prominent Journals in which Electroanalytical Research is Published

Journal of Electroanalytical Chemistry

Analytical Chemistry

Electrochimica Acta

Journal of the Electrochemical Society

Bulletin of the Chemical Society of Japan

Journal of the American Chemical Society

Journal of Physical Chemistry

3. Solutions to Study Problems

1-B. According to equation (B-7)

$$-\frac{dC^b}{dt} = \left(\frac{AD}{\delta V}\right) \times C^b$$

Let $k = \left(\frac{AD}{\delta V}\right)$

So $-\frac{dC^b}{dt} = kC^b$ or $-d\,\ell n\, C^b = k\,dt$

The solution to this differential equation is

$$\ell n\, C^b = -kt + \text{constant.}$$

The constant is evaluated from the fact that at $t = 0$, $C^b = C_0^b$ where C_0^b is the initial concentration. Thus

$$\ell n\, C^b = -kt + \ell n\, C_0^b$$

or $$C^b = C_0^b \exp(-kt)$$

2-B. a. The solution contains

$$0.1 \text{ moles}/\ell \times 0.1\ \ell = 10^{-2} \text{ moles of } Cu^{2+}$$

2 Faradays of charge are required per mole of Cu^{2+} for reduction to Cu^0. Therefore

$$2 \times 10^{-2} \times F = 2 \times 10^{-2} \times 96,484 = 1929.7 \text{ coulombs}$$

b. Faradaic efficiency is calculated from equation (B-2)

$$\text{Efficiency} = \frac{2 \times 10^{-2} \times F}{2000} = \frac{1929.7}{2000} = 96.5\%$$

c. 100 milliamperes for 50 minutes $\Rightarrow 10^{-1} \times 50 \times 60 = 300$ coulombs. The faradaic efficiency of 98% means that $0.98 \times 300 = 294$ coulombs resulted in the deposition of copper. To consume all of the Cu^{2+}, 1929.7 coulombs are required (part a). Therefore the fraction of Cu^{2+} remaining will be

$$\left(\frac{1929.7 - 294}{1929.7}\right) = 0.848.$$

The concentration of Cu^{2+} is therefore

$$0.848 \times 10^{-1} = .0848 \text{ M}.$$

3-B. The cell shown in A-3 is a single-compartment cell in which the working and auxiliary electrodes are both exposed to the same solution. As copper is plated onto the working electrode according to

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

the electrode reaction proceeding at the auxiliary electrode will be

$$H_2O \longrightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^-$$

Thus the total cationic charge in the solution does not change because each Cu^{2+} ion that is removed is replaced by two H^+ ions.

4-B. a.
$$\begin{array}{rl} & N_2H_4 \longrightarrow N_2 + 4H^+ + 4e^- \\ 4H_2O + 4e^- & \longrightarrow 2H_2 + 4OH^- \\ \hline & N_2H_4 \longrightarrow N_2 + 2H_2 \end{array}$$

b. 1 liter of gas at S.T.P. is 1/22.4 moles of $N_2 + H_2$. Each faraday of charge according to part a produces 1/4 mole N_2 plus 1/2 mole H_2 or 3/4 mole of gas. To produce 1/22.4 moles of gas will require $1/22.4/3/4 = 0.0595$ faradays or $0.0595 \times 96,484 = 5743$ coulombs.

5-B.  $+ \frac{1}{2}H_2$

So the products are aniline and hydrogen. Almost any other combination of products would require more charge. (See the cited reference for a detailed discussion.)

1-C. 5×10^{-3} amp $\times$ 250 sec = 1.25 coulombs

$$\frac{1.25 \text{ coul}}{96,484 \text{ coul/equiv}} = 1.295 \times 10^{-5} \text{ equiv}$$

Thus, for reactants that consume one Faraday per mole ca. 13 micromoles would be present.

2-C. According to the data given, the limiting current density corresponding to $Br^- \rightarrow \frac{1}{2}Br_2 + e^-$ for a 0.1 M (= 100 millimolar) solution of NaBr would be 0.5×10^2 = 50 milliamp cm^{-2}.

10 milliamp at a 0.5 cm^2 electrode therefore corresponds to 2/5 of the limiting current and a faradaic efficiency of 100% is assured since the oxidation of Br^- under these conditions occurs at potentials where there is negligible contributions from the likely interefering reaction, the oxidation of water. 30 milliamp at the same electrode exceeds the limiting current density so that a second electrode reaction would have to proceed in order for the current to pass. $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ is the most likely second reaction and the oxidant generated in this way, oxygen, may escape from the solution without reacting with As(III). Positive errors therefore result.

3-C. According to the titration reaction, 1.5 moles of BrO^- must be generated for each mole of NH_3. The generation of BrO^- involves 2 Faradays per mole:

$$Br^- + H_2O \longrightarrow BrO^- + 2H^+ + 2e^-$$

Therefore 1 micromole of NH_3 will require $10^{-6} \times 1.5 \times 2 = 3 \times 10^{-6}$ Faradays of charge = $3 \times 10^{-6} \times 96,484$ coulombs. With a current of 4×10^{-3} amp the time required is

$$\frac{3 \times 96,747 \times 10^{-6}}{4 \times 10^{-3}} = \underline{72.37 \text{ sec}}.$$

1-D. a. The flux is calculated from Fick's First Law, namely

$$f_x = D\left(\frac{\partial C}{\partial x}\right)_x \text{ moles/cm}^{-2}\,\text{sec}^{-1}$$

b. Similarly,

$$f_{x+dx} = D\left(\frac{\partial C}{\partial x}\right)_{x+dx}$$

c. $$dC = \frac{(f_{x+dx} - f_x)\, A\, dt}{\underbrace{A\, dx}_{\text{volume of layer}}}$$

(Cross-sectional area of layer)

$$dC = \frac{(f_{x+dx} - f_x)\, dt}{dx}$$

d. $$f_{x+dx} = f_x + \left(\frac{\partial f_x}{\partial x}\right) dx = D\left(\frac{\partial C}{\partial x}\right)_x + \frac{\partial}{\partial x} D\left(\frac{\partial C}{\partial x}\right)_x$$

$$dC = \frac{\left[D\left(\frac{\partial C}{\partial x}\right)_x + \frac{\partial}{\partial x} D\left(\frac{\partial C}{\partial x}\right)_x - D\left(\frac{\partial C}{\partial x}\right)_x\right] dt}{dx}$$

so $$\frac{dC}{dt} = D\frac{\partial^2 C}{\partial x^2}$$ which is Fick's Second Law (equation D-2).

2-D. a. We can take advantage of the fact that $it^{1/2}$ is constant in chronoamperometry (cf. D-7). Thus $(55)(10^{-2})^{1/2} = i\,(10^2)^{1/2}$

$$i = \frac{5.5}{10} = 0.55 \text{ ma. after 100 sec}$$

$$i = \frac{5.5}{10^2} = 0.055 \text{ ma. after } 10^4 \text{ sec}$$

b. The diffusion coefficient and electrode area are not specified. However, from the relationship between the equations governing chronoamperometry and chronocoulometry we have

$$it^{1/2} = \frac{nFAC^bD^{1/2}}{\pi^{1/2}} = \text{const.}$$

and $$Q = \frac{2nFAC^bD^{1/2}t^{1/2}}{\pi^{1/2}}$$

Thus,

$$Q = 2(it^{1/2})t^{1/2}$$

($it^{1/2}$: chronoamperometric constant; $t^{1/2}$: chronocoulometric time)

Since $it^{1/2} = 5.5$ ma $\text{sec}^{1/2}$

$$Q = 2 \times 5.5 \times (10^2)^{1/2} = 110 \text{ ma sec after } 10^2 \text{ sec or } 0.10 \text{ coulomb}$$

To reduce 0.1 liter of a 0.01 M solution of an oxidant by 2 electrons requires

$$0.1 \times 10^{-2} \times 2 \times 96,487 = 193 \text{ coulombs}$$

$\therefore$ the fraction reduced after 10^2 seconds is $\frac{0.10}{193} = 0.052\%$

c. The currents decay to small values because the layer of solution next to the electrode surface is depleted of reactant long before the bulk of the solution. At this point the current is limited (in unstirred solutions) by the rate of diffusion of additional reactant across the depleted layer to the electrode surface.

3-D. The Cottrell Equation, (D-6), gives the current-time behavior during chronoamperometric experiments in which the current is limited by linear diffusion. It is convenient to rewrite eqn. D-6 in the form

$$it^{1/2} = \frac{nFAC^b D^{1/2}}{\pi^{1/2}}$$

The problem says IO_3^- is reduced to I^- (via $IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^-$) so that n = 6. A = 0.1 cm^2 and $C^b = 10^{-4}$ M. Thus,

$$it^{1/2} = \frac{6 \times 96,484 \times 0.1 \times 10^{-4} \cdot D^{1/2}}{\pi^{1/2}}$$

$$it^{1/2} = 3.26\, D^{1/2}$$

The set of current-time data given in the problem yield the following set of values for $it^{1/2}$: 340, 342, 340, 338, 344, 339 and 340 milliamp $(millisec)^{1/2}$. The average of these seven values is 341 milliamp $(millisec)^{1/2}$ or 0.01078 ampere $(sec)^{1/2}$.

Thus, $D^{1/2} = \frac{0.01078}{3.26} = 3.308 \times 10^{-3}$

and $D = 1.09 \times 10^{-5}\ cm^2\ sec^{-1}$.

4-D. a. On 1 cm^2 there will be 10^{+14} molecules cm^{-2}.

$$\frac{10^{+14} \text{ molecules cm}^{-2}}{6.02 \times 10^{23} \text{ molecules mole}^{-1}} = 1.66 \times 10^{-10} \text{ mole cm}^{-2}$$

$$\text{Charge} = 1.66 \times 10^{-10} \text{ moles cm}^{-2} \times 2F \text{ coulombs mole}^{-1}$$

$$= 1.66 \times 10^{-10} \times 2 \times 96,484 = 3.21 \times 10^{-5} \text{ coulombs}$$

$$= 32.1 \text{ microcoulombs cm}^{-2}$$

b. The charge consumed by diffusing molecules is calculated from the integral of the Cottrell equation (eqn. D-15)

$$Q = \frac{2nFAC^b D^{1/2} t^{1/2}}{\pi^{1/2}}$$

$$\frac{Q}{A} = \text{charge cm}^{-2} = (9.74 \times 10^{-4})\, t^{1/2} \text{ coulomb cm}^{-2}$$

At $t = 10^{-2}$ sec, $\frac{Q}{A} = 97.4$ microcoulomb cm^{-2}

At $t = 10^{-1}$ sec, $\frac{Q}{A} = 308$ microcoulomb cm^{-2}

At $t = 1$ sec, $\frac{Q}{A} = 974$ microcoulomb cm^{-2}

c. As is clear from part b, the contribution to the intercept of a chronocoulometric plot of charge *vs* $(\text{time})^{1/2}$ from adsorbed reactant becomes a smaller fraction of the total charge the longer the duration of the experiment. For this reason better accuracy results if the charge-time data are collected as rapidly as the available instrumentation allows.

1-E. a. The Sand equation (E-5) can be applied in rearranged form:

$$(D)^{1/2} = \frac{2\, i \tau^{1/2}}{(\pi)^{1/2} nF A C^b}$$

$$\frac{i}{A} = 0.46 \times 10^{-3} \text{ amp cm}^{-2}$$

$$\tau = 25 \text{ sec}$$

$$n = 2 \text{ for } Cu^{2+} + 2e^- \rightarrow Cu$$

$$nF = 2 \times 96,484 \text{ coulombs mole}^{-1}$$

$$C^b = 5 \times 10^{-6} \text{ moles/cm}^3$$

Substituting:

$$D^{1/2} = \frac{2 \times 0.46 \times 10^{-3} \times (25)^{1/2}}{(\pi)^{1/2} \times 2 \times 96,484 \times 5 \times 10^{-6}} = 2.69 \times 10^{-3}$$

$$D = 0.72 \times 10^{-5} \text{ cm sec}^{-1}$$

b. If the product of the electrode reaction were soluble in the solution or the electrode (e.g., at Hg electrodes a soluble amalgam would be formed) it would be free to diffuse away from the electrode and the reverse transition time would be given by eqn. (E-9)

$$\tau_r = \tfrac{1}{3} t_f \quad \text{or} \quad 7 \text{ sec.}$$

However, since the Cu^{2+} is reduced to copper metal which deposits on the solid platinum electrode all of the deposited copper will be re-oxidized following the current reversal so that $\tau_r = t_f$ or 21 seconds.

2-E. a. Figure E-20 requires that the ratio τ_r/t_f be known. The problem states that $t_f = 5.5$ sec and $\tau_r = 0.95$ sec so

$$\tau_r/t_f = 0.173 .$$

From Figure E-20 this value corresponds to a value of $k_f t_f$ of 0.906 therefore $k_f = \frac{.906}{5.5} = 0.16 \text{ sec}^{-1}$.

b. If $t_f = 12$ sec, $k_f t_f = 1.98$ and, from Figure E-20, $\tau_r/t_f = 0.11$. So

$$\tau_r = 0.11 \times 12 = 1.32 \text{ sec.}$$

1-F. From equation (F-5)

$$E_{p_C} = E^0_{ox, red} - \frac{0.029}{n}\left[1 + \log\frac{D_{ox}}{D_{red}}\right]$$

Since $D_{ox} = D_{red}$

$$E_{p_C} = E^0_{ox, red} - 0.029 \text{ volt}$$

Applying the Nernst equation at E_{p_C}:

$$E_{p_C} = E^0_{ox, red} - 0.059 \log\frac{[Red]}{[Ox]}$$

$$\therefore \; -0.059 \log\frac{[Red]}{[Ox]} = -0.029$$

$$\frac{[Red]}{[Ox]} = 10^{1/2} = 3.16$$

2-F. We apply the Randles-Sevčik equation (F-4):

$$i_p = 269\, n^{3/2} A D^{1/2} \nu^{1/2} C^b$$

$$\frac{i_{p_{Tl^+}}}{i_{p_{Cu^{2+}}}} = 1 = \frac{(1)^{3/2}}{(2)^{3/2}} \cdot \left(\frac{2 \times 10^{-5}}{0.72 \times 10^{-5}}\right)^{1/2} \frac{(1)^{1/2}}{\nu^{1/2}} \frac{3 \times 10^{-3}}{1 \times 10^{-4}}$$

$$\nu^{1/2} = \frac{(2 \times 10^{-5})^{1/2} (3 \times 10^{-3})}{(2)^{3/2} (0.72 \times 10^{-5})^{1/2} (10^{-4})} = 17.6$$

$$\nu = 312.5 \text{ volts sec}^{-1}$$

3-F. This question requires both the Randles-Sevčik equation (F-4) and the Cottrell equation (D-6). Dividing one equation by the other gives:

$$\frac{i_p}{(it^{1/2})} = \frac{2.69 \times 10^5 \, (n)^{1/2} \, \nu^{1/2}}{F/\pi^{1/2}}$$

A, $D^{1/2}$, C^b all cancel and are therefore not needed.

Hence

$$it^{1/2} = \frac{i_p F}{(\pi)^{1/2} \cdot 2.69 \times 10^5 \cdot (n)^{1/2} \, (\nu)^{1/2}}$$

$$= \frac{85 \times 10^{-6} \cdot 96,487}{(\pi)^{1/2} \, 2.69 \times 10^5 \cdot (2)^{1/2} \cdot (0.2)^{1/2}}$$

$$= 2.71 \times 10^{-5} \text{ amp sec}^{1/2}$$

4-F. At sufficiently high scan rates reaction (F-14) has no chance to proceed from left to right during the scan so that the concentrations of the reactants and products are effectively "frozen". At this point curve B becomes linear again with a slope corresponding to the low initial concentration of Cd^{2+} that is present at equilibrium.

1-G. The two patterns are consistent with a single, two-electron reduction and oxidation in H_2SO_4 [$Cu^{2+} + 2e^- \overset{Hg}{\rightleftharpoons} Cu(Hg)$] and two one-electron reductions and oxidations in HCl [$Cu^{2+} + e^- \overset{HCl}{\rightleftharpoons} CuCl_2^-$; $CuCl_2^- + e \overset{Hg}{\rightleftharpoons} Cu(Hg) + 2Cl^-$]

2-G. a. From equation (G-4)

$$E^0_{ox,\,red} = \frac{E_{p_a} + E_{p_c}}{2} + 0.029 \log \frac{D_{ox}}{D_{red}}$$

If we neglect the difference between D_{ox} and D_{red} (usually a good approximation for aromatic hydrocarbons and their radical ions) we have

$$E^0_{R^+,\,R} = \frac{1060 + 1120}{2} = 1090 \text{ mV}$$

$$E^0_{R,\,R^-} = \frac{-1160 + (-1100)}{2} = -1130 \text{ mV}$$

b. To convert a difference in standard potentials into a free energy difference it is necessary to use the thermodynamic formula relating these two quantities, namely $\Delta G^0 = -n\,\Delta E^0$, where ΔG^0 is the free energy difference in electron volts. Thus,

$$\Delta G^0 = 1.090 - (-1.130) = 2.220 \text{ electron volts}$$

$$2.22 \text{ eV} \times 23.07 \text{ kcal mole}^{-1} \text{ eV}^{-1} = 51.2 \text{ kcal mole}^{-1}$$

This is a large amount of released energy and it is therefore not surprising that in many instances the reaction between anion and cation radicals of aromatic hydrocarbons is accompanied by the emission of light. Active research is now being conducted in the field of electrochemiluminescence whereby electrical energy is converted into light by electrochemical means.

1-H. Because the area of the dropping mercury electrode oscillates as each drop grows and detaches from the capillary and because the concentration of the reactant in the solution near the electrode surface decreases during the lifetime of each drop.

2-H. The capacitance of the electrode-electrolyte interface increases with the drop area and a continuous flow of charge is required at constant potential to charge this growing capacitance. A second factor contributing to residual currents is the presence of residual electroactive impurities such as oxygen in the electrolyte solutions.

3-H. a. The Ilkovič equation (H-10) is called for:

$$i_d = 708\, n D^{1/2} C^b m^{2/3} t^{1/6}$$

$$i_d = 708 \times 2 \times (1 \times 10^{-5})^{1/2} \times 1 \times (2.5)^{2/3} \times (3)^{1/6}$$

$$= 9.88 \text{ microamp}$$

b. The current just before drop fall is 9.88 microamp.
The drop volume, V, at this point is $\frac{mt}{\rho}$ because mt is the drop weight and ρ is the density of mercury (i.e., 13,600 mg/cm^3)
The drop radius is therefore

$$r = \left(\frac{V}{4/3\,\pi}\right)^{1/3} = \left(\frac{mt}{\rho(4/3)\,\pi}\right)^{1/3}$$

and the drop area, A, is

$$A = 4\pi r^2 = 4\pi\left(\frac{mt}{\rho\, 4/3\,\pi}\right)^{2/3}$$

Finally, the current density is

$$\frac{i}{A} = \frac{9.88}{A} = \frac{9.88}{4\pi(\frac{mt}{\rho\, 4/3\,\pi})^{2/3}} = 304 \cdot \text{microamp cm}^{-2}$$

c. A general formula for current density can be obtained by dividing the Ilkovič current by the drop area:

$$\frac{i_d}{A} = \frac{708\, n D^{1/2} C^b m^{2/3} t^{1/6}}{4\pi\left(\frac{mt}{\rho(4/3)\pi}\right)^{2/3}} = \frac{708\, n D^{1/2} C^b}{\frac{4\pi}{(4/3\,\pi\rho)^{2/3}}}\, t^{-1/2}$$

Thus, the current density does change during drop growth--it varies as $t^{-1/2}$, becoming smaller and smaller during drop growth.

d. $\frac{i_d}{A}$ at t = 2 sec:

$$\frac{i_d}{A} = \frac{708 \times 2 \times (1 \times 10^{-5})^{1/2} \times 1 \times (2)^{-1/2}}{4\pi/(\frac{4\pi\rho}{3})^{2/3}} = 372 \cdot \text{microamp cm}^{-2}$$

4-H. Equation (H-15) can be used to solve this problem. $C_s = 2 \times 10^{-4}$ M, $V_s = 1$ ml, $V_u = 25$ ml, $(i_d)_u = 0.14\ \mu$A, $(i_d)_s = 0.32\ \mu$A. Substituting in eqn. (H-15) gives

$$Cu = \frac{2 \times 10^{-3} \times 1 \times 0.14}{(25+1) \times 0.32 - 25 \times 0.14}$$

$$= \frac{2.8 \times 10^{-4}}{8.32 - 3.50} = \frac{2.8 \times 10^{-4}}{4.82}$$

$$= 5.8 \times 10^{-5} \text{ M}$$

5-H. The slope of a plot of $E_{d.m.e.}$ *vs* $\ell n \frac{i}{i_d - i}$ (see H-20) is $\frac{RT}{nF} = \frac{25.6}{n}$ mV. The value of 12.8 tells us that n = 2. The slope of a plot of $E_{d.m.e.}$ *vs* $\ell n[NH_3]$ is $\frac{RT}{nF}p$. Since we know $\frac{RT}{nF} = 12.8$ mV, p = 4, so $Cd(NH_3)_4^{2+}$ is the predominating species.

6-H. Using equation (H-36)

$$\Delta E_{1/2} = (-0.784) - (-0.587) = \frac{RT}{nF}\left[\ell n \left(\frac{D_{Cd^{2+}}}{D_{Cd(NH_3)_4^{2+}}}\right)^{1/2} - p\ \ell n[NH_3] - \ell n\ K_{eq}\right]$$

For $\frac{D_{Cd^{2+}}}{D_{Cd(NH_3)_4^{2+}}} = 1$ and $[NH_3] = 1\ M$

$$0.206 = \frac{RT}{nF} \ell n\, K_{eq} \qquad K_{eq} = 9.6 \times 10^6$$

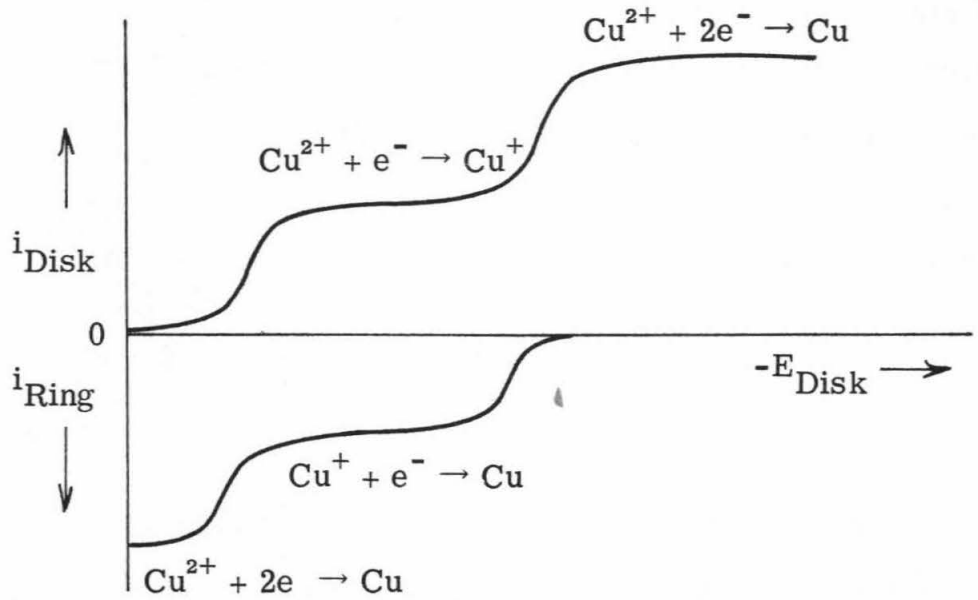
1-J. In d.c. polarography the changing area of the dropping electrode causes the charging current. In normal pulse polarography the sudden steps in the electrode potential produce the transient charging current. (The electrode area is virtually constant during the brief period when the current is observed.)

2-J. The determination of minor solution components which are reduced at more negative potential than major components is facilitated. Two species which are reduced at nearby potentials are more easily resolved in the differential mode.

3-J. The material to be subsequently anodically stripped is collected in mercury electrodes. Hg^{2+} would be reduced to mercury metal during the plating stage and would be indistinguishable from the bulk of the electrode. (It might be feasible to use another electrode material, such as carbon to determine Hg^{2+} by depositing Hg^0 and subsequently stripping it off anodically. However, the deposition and re-dissolution of traces of metals from solid electrodes is known to be fraught with difficulties.)

O_2 and IO_3^- are reduced to products (H_2O and I^-, respectively) which do not deposit on the mercury electrode. They can, therefore, not be subsequently stripped off anodically.

1-K.


$Cu^{2+} + 2e^- \rightarrow Cu$
$Cu^{2+} + e^- \rightarrow Cu^+$
i_{Disk}
0
i_{Ring}
$-E_{Disk}$
$Cu^+ + e^- \rightarrow Cu$
$Cu^{2+} + 2e \rightarrow Cu$

About the Lecturer

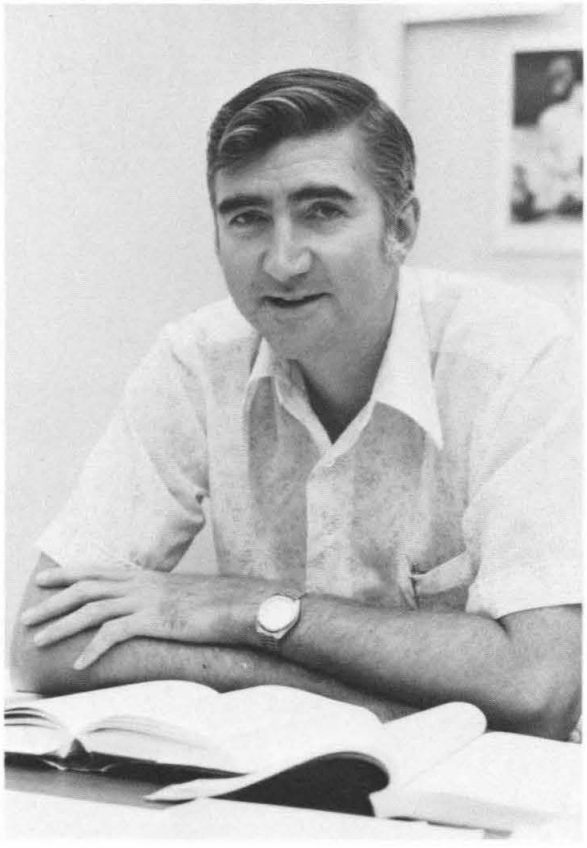


Photo: Floyd Clark, Caltech.

Fred Anson received his B.S. degree from California Institute of Technology in 1954 and his Ph.D. from Harvard University in 1957. He has been on the faculty at Caltech since 1957 and is presently Professor and Executive Officer for Chemistry. He has been a Guggenheim Fellow at the Free University of Brussels, a Fulbright Research Scholar at the University of Florence, and an Alfred P. Sloan Foundation Fellow.